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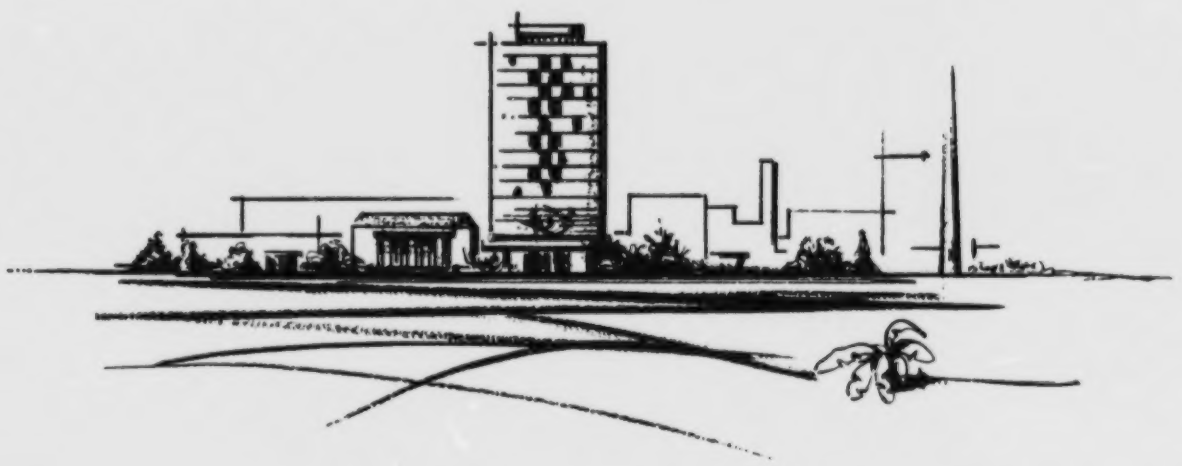

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FINAL REPORT

on

FUNDAMENTAL STUDY OF SULFUR FIXATION BY LIME AND MAGNESIA

to

ROBERT A. TAFT SANITARY ENGINEERING CENTER
PUBLIC HEALTH SERVICE, BSS-EH
DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

June 30, 1966

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FUNDAMENTAL STUDY OF SULFUR FIXATION BY LIME AND MAGNESIA

June 30, 1966

OBJECTIVES

This study was undertaken ~~by Battelle~~ to identify the basic factors involved in the capsure of SO_2 by limestone or dolomite added with the fuel or blown separately into the hot flue gas of central-station boiler furnaces. It has been known for many years that lime and magnesia will react with SO_2 to form calcium and magnesium sulfates in boiler furnaces, but the basic limiting conditions under which these reactions can occur have never been adequately defined. It was the objective of this brief study to provide that information.

The report is in three parts, following a brief introduction: thermodynamic considerations, kinetics, and recommendations for use in the field. An extensive appendix tabulates the results of the many thermochemical calculations made during this study.

INTRODUCTION

Presently the major consumer of solid fuels in the United States, public utilities in 1965 burned 243 million tons of bituminous coal to generate the largest part of the electricity that powers our economy. Residual fuel oil provided about one-ninth as much equivalent energy for electrical generation. Although the stacks of large public-utility power plants usually are high to distribute the products of combustion over a wide area – the recently announced Conemaugh station will have 1000-foot stacks – sulfur dioxide present in flue gas can still contribute markedly to wide-scale air pollution. For instance, if the sulfur content of the utilities' coal supply and their residual fuel in 1965 averaged 3 percent, the amount of SO_2 emitted by power plants over the year would have come to more than 15 million tons, assuming 95 percent conversion of the sulfur in the fuel to SO_2 appearing in the stack gas. Although more troublesome from some standpoints, SO_3 emission is much less, usually amounting to only 1 percent of the SO_2. Burning oil with low excess air reduces even this small amount of SO_3 essentially to zero, but low excess air does not decrease the problem with SO_2.

Loading the air we breathe with this tremendous tonnage of SO_2 is causing increasing concern among those who watch over public health, particularly because the utilities double their output of electricity every 10 years. Sulfur dioxide from power plants, too, would then double every 10 years. Coupled with a gradually increasing sulfur content in fuels, great concern is being expressed for the quality of our atmosphere in the years ahead. As a result, laws restricting the sulfur content of fuels have begun to appear in many localities. Coal producers and public utilities have teamed up to seek feasible and economically suitable procedures for removing sulfur from coal, and oil refiners have sought practical means of desulfurizing residual fuel. So far, no economically attractive schemes have been found. Generally, costs of removing sulfur from fuels are excessively

high, and no assured scheme for providing low-sulfur fuels has been turned up. Limiting the sulfur in fuels provides one way of controlling SO_2 emission, and this has been the objective of many ordinances. It may be a relatively costly one, however, if limiting the sulfur content calls for expensive processing of fuels or for radical changes in sources of fuel supply.

An alternative method of decreasing the SO_2 output from stacks is to remove a large part of the sulfur oxides from the flue gases. Considerable attention has been given this problem for many years, ranging from wet scrubbing of the flue gas as at Battersea and Bankside stations in London beginning three decades ago to the catalytic conversion of SO_2 to SO_3 and its removal from the flue gas as an acid mist at normal stack temperatures. Adsorption on solid particles, reaction with ammonia, chemical scrubbing, and bag filters combined with an additive are examples of other systems proposed to remove sulfur oxides from flue gases.

The procedure considered here, one that has been brought up from time to time over the past 30 years, is the addition of limestone or dolomite to a furnace such that $CaSO_4$ or $MgSO_4$ and other solids would be the end product rather than SO_2. It has long been known for example, that coals containing large amounts of calcite and pyrite give trouble in the analytical determination of ash in coal. In such cases, the ash appears high because appreciable quantities of calcium sulfate are formed when the coal is heated in a muffle. Hence ASTM specifies that such coals are to be ashed by a procedure where the pyritic sulfur is oxidized and the SO_2 is expelled before the calcite is decomposed. (1) Lignite and brown coal, usually containing large amounts of calcite, generally trap sulfur when burned, so that the ash from these fuels frequently contains as much as 30 percent SO_3. (2) It is this ability of lime to react with SO_2 under some conditions that makes it so interesting as a means of decreasing the SO_2 in flue gas.

The chemical reactions involved here are relatively simple. Yet no clear insight has been available as yet on which reactions predominate or how the reactions are influenced by conditions within the furnace. In particular, there has been little or no information available on the relative effectiveness of limestone and dolomite, on the influence of temperature, on the presence of ash, and on the time required for trapping SO_2 by these solids under furnace conditions. Hence this study was made to evaluate the potential usefulness of this means of decreasing SO_2 emission from power plants.

Three tasks were involved:

- Thermodynamic calculations to show the course of the probable chemical reactions
- Kinetic factors as far as they can be deduced without experimentation
- Recommendations for the use of limestone and dolomite most effectively in large central-station boiler furnaces.

This report contains the results of these calculations and evaluations to aid those seeking practical and economical means of minimizing SO_2 emissions. It will also serve

(1) Sampling and Analysis of Coal and Coke, ASTM, D-271, Part 19, p 23, 1966.
(2) Sondreal, E. A., Kube, W. R., and Elder, J. L., "Characteristics and Variability of Lignite Ash From the Northern Great Plains Province", 1965 Lignite Symposium, Bismarck, N. D., p 12.

as a broad guide in evaluating proposed large-scale tests in boiler furnaces where conditions cannot always be accurately defined. The calculations here are based on single systems. A much more complicated procedure would be necessary for interrelated systems where one process would be interacting with another. For the present state of the art, the simplified methods used here should be entirely satisfactory and can serve later as the starting point if a more elaborate treatment should ever be desirable.

It should be emphasized at the outset of this report that the conclusions reached here are based on sound but limited theoretical considerations, and that theory at best can point only to expected results. Experimentation, eventually on a large scale, will be necessary to establish the conditions where this method of decreasing SO_2 emission is most effective.

CHEMICAL THERMODYNAMIC CONSIDERATIONS

by

J. J. Ward and D. A. Pettit

A chemical thermodynamic study was made, as the first step in this study, of reactions of $CaCO_3$, $MgCO_3$, and dolomite with $SO_2(g)$ and $O_2(g)$ in boiler atmospheres at temperatures up to 3000 F. The purpose here was to collect from the literature basic data required to evaluate schemes for fixing sulfur with limestone, dolomite, $CaCO_3$, CaO, $MgCO_3$, and MgO. Interfering reactions that may occur from silica or alumina in the coal ash were included. All these basic thermochemical data have now been collected and interpreted as they apply to the sulfur-fixing problem. "Thermochemical" in this report is used in the same sense as "Chemical Thermodynamics".

As a first step in this work, standard free-energy changes of reactions of interest were tabulated from literature sources at 100 F intervals from 300 to 2000 F, at 2500 F, and at 3000 F. From the value of the standard free energy change of a reaction, ΔF_R°, the logarithm of the equilibrium constant of the reaction was calculated. Thermochemical data for the pertinent reactions are collected in the Appendix in Tables A-1 through A-19 with references to the literature sources. A listing of the reactions given in the tables is shown on page A-1.

These calculations are based on bulk properties. Some surface effects might be expected because the solids would be pulverized, but the difference attributable to this increase in surface area would be negligibly small.

A negative value of the standard free energy change of a reaction, ΔF_R°, shows the tendency or driving force for the reaction to occur. The ΔF_R° value, however, gives no information on the rate of reaction nor the time necessary for its completion. A review of that part of the problem is given in the next section of this report. The equilibrium constant, also a measure of extent of reaction, is useful in calculating the conversion under non-standard-state conditions, such as those existing in boiler atmospheres. A somewhat detailed example follows on the application of these data to $SO_2(g)$ removal from a boiler atmosphere by lime. A tabulation will be given of the temperature effect on SO_2 removal.

In Table A-1, thermochemical data are listed for the reaction of lime, SO_2, and O_2 to form $CaSO_4$. This reaction is:

$$CaO(c) + SO_2(g) + \frac{1}{2}\, O_2(g) = CaSO_4(c). \qquad (1)$$

From the value of ΔF_R°, the logarithm of the equilibrium constant, $\log_{10} K$, may be calculated as

$$\log_{10} K = \frac{-\Delta F_R^\circ}{4.576T}, \qquad (2)$$

where

ΔF_R° = calories for the reaction

T = absolute temperature, °K.

The equilibrium constant, K, may be written for Reaction (1) as,

$$K = \left(\frac{a_{CaSO_4}}{a_{CaO}}\right) \cdot \frac{1}{P_{SO_2(g)} P_{O_2}^{1/2}(g)} , \qquad (3)$$

where a_{CaSO_4} and a_{CaO} are Raoultian activities of the solids calcium sulfate and lime. These solids are usually assumed to be at unit activity. As will be discussed later, this assumption is not valid in the decomposition of dolomite nor in the interaction of CaO with ash components.

Here $p_{SO_2}(g)$ and $p_{O_2}(g)$ are the partial pressures of $SO_2(g)$ and $O_2(g)$ in atmospheres.

Equation (3) can be expressed as

$$K = \left(\frac{a_{CaSO_4}}{a_{CaO}}\right) \cdot \frac{1}{X_{SO_2(g)} \cdot X_{O_2}^{1/2} P^{3/2}} , \qquad (4)$$

where $X_{SO_2(g)}$ and $X_{O_2(g)}$ are the mole fractions in the gas phase of sulfur dioxide and oxygen gas. Equation (4) can be written at 1-atmosphere pressure as:

$$X_{SO_2(g)} = \left[\frac{a_{CaSO_4}}{a_{CaO}}\right] \cdot \frac{1}{K X_{O_2}^{1/2}} . \qquad (5)$$

The mole fraction, $X_{SO_2(g)}$ can be expressed as:

$$\text{percentage by volume } SO_2 = 10^{+2} X_{SO_2(g)}$$

and

$$\text{ppm } SO_2(g) = 10^{+6} X_{SO_2(g)} .$$

Similar equations can be derived for the reactions of MgO, SO_2, and O_2 to form $MgSO_4$.

Desulfurizing Action of CaO(c) and MgO(c) in Flue Gas

By applying the data of Tables A-1 and A-2 according to the above method, the equilibrium concentration of $SO_2(g)$ in flue gas can be calculated as a function of temperature at a level of 2.7 percent O_2 in the flue gas for CaO and MgO, assuming unit activity of solids.

TABLE 1. EQUILIBRIUM CONCENTRATION OF $SO_2(g)$ IN PARTS PER MILLION (PPM) OF FLUE GAS CONTAINING 2.7 PERCENT O_2, AND WITH UNIT ACTIVITY OF SOLIDS

Temperature, F	SO_2, ppm	
	CaO Fixation of Sulfur	MgO Fixation of Sulfur
1000	1.7×10^{-11}	1.3×10^{-3}
1200	1.1×10^{-7}	1.0
1400	1.0×10^{-4}	180
1600	2.3×10^{-2}	$1.1 \times 10^{+4}$
1800	1.95	$3.2 \times 10^{+5}$(a)
2000	74.8	($>10^{+6}$)(b)
2500	$6.3 \times 10^{+5}$(a)	
3000	($>10^{+6}$)(b)	

(a) Insufficient sulfur in coal to approach this equilibrium value of $SO_2(g)$ in flue gas.
(b) Implies greater than 100 percent SO_2 required for equilibrium.

An examination of the above table indicates that, thermochemically, sulfur removal by CaO is limited to temperatures below about 2250 F and by MgO to less than about 1550 F under boiler atmosphere conditions. The assumption that the activity ratios,

$$\left(\frac{a_{CaSO_4}}{a_{CaO}}\right) \text{ and } \left(\frac{a_{MgSO_4}}{a_{MgO}}\right),$$

are unity is a good one if limestone or magnesite are used as reactants, and if excessive ash constituents are not included. Surface effects would appear in the term a_{CaO} which would be greater than unity, resulting in a decrease in the equilibrium level of SO_2 in contact with the solid. As noted earlier, however, the effect is so small as to be disregarded for solids ground to a practical particle size.

Calcination of Limestone

Some consideration has been given to the thermochemical calcination of limestone, and to the desulfurizing action of limestone directly without formation of CaO. Thermochemical data are reported for the calcination of $CaCO_3$. From these data, the dissociation pressure of $CaCO_3$ can be calculated at 1-atmosphere pressure as shown in Table 2.

TABLE 2. DISSOCIATION OF LIMESTONE IN FURNACE FLUE GAS

$$[CaCO_3(c) \rightleftharpoons CaO(c) + CO_2(g)]$$

Temperature, F	Equilibrium Concentration of CO_2 in Flue Gas, percentage by volume
1000	0.05
1200	3.5
1400	12.1

Because flue gas contains typically about 14.5 percent CO_2 by volume, these data show that CaO will tend to recombine with CO_2 in boiler atmospheres at temperatures below about 1415 F. Figure 1 shows this situation graphically. In other words, below 1415 F, CaO is not stable because of the combustion atmosphere, and $CaCO_3$ would be formed at the expense of any CaO.

For this reason, the desulfurizing action of $CaCO_3$ below 1400 F becomes important. Table 3 shows the extent of this factor as calculated from basic data taken from Table A-10.

TABLE 3. DESULFURIZING ACTION OF UNCALCINED LIMESTONE

$$[CaCO_3(c) + SO_2(g) + \frac{1}{2} O_2(g) \rightleftharpoons CaSO_4(c) + CO_2(g)]$$

Temperature, F	Equilibrium Concentration of SO_2, ppm, With 2.7 Percent O_2 in Flue Gas and Unit Activity of Solids
1000	4.5×10^{-9}
1200	1.4×10^{-6}
1400	1.2×10^{-4}

These calculations predict that limestone can desulfurize flue gas up to its calcination temperature. However, the data indicate thermodynamic feasibility only; no interpretation can be made concerning reaction kinetics nor the time required for the equilibrium values to be reached.

Stability of Dolomite

The thermochemical stability of dolomite is shown in Table A-13. These data indicate that dolomite dissociates at 865 F to exert a partial pressure of 1 atmosphere according to the reaction:

$$CaCO_3 \cdot MgCO_3(c) \rightleftharpoons CaCO_3(c) + MgO(c) + CO_2(g).$$

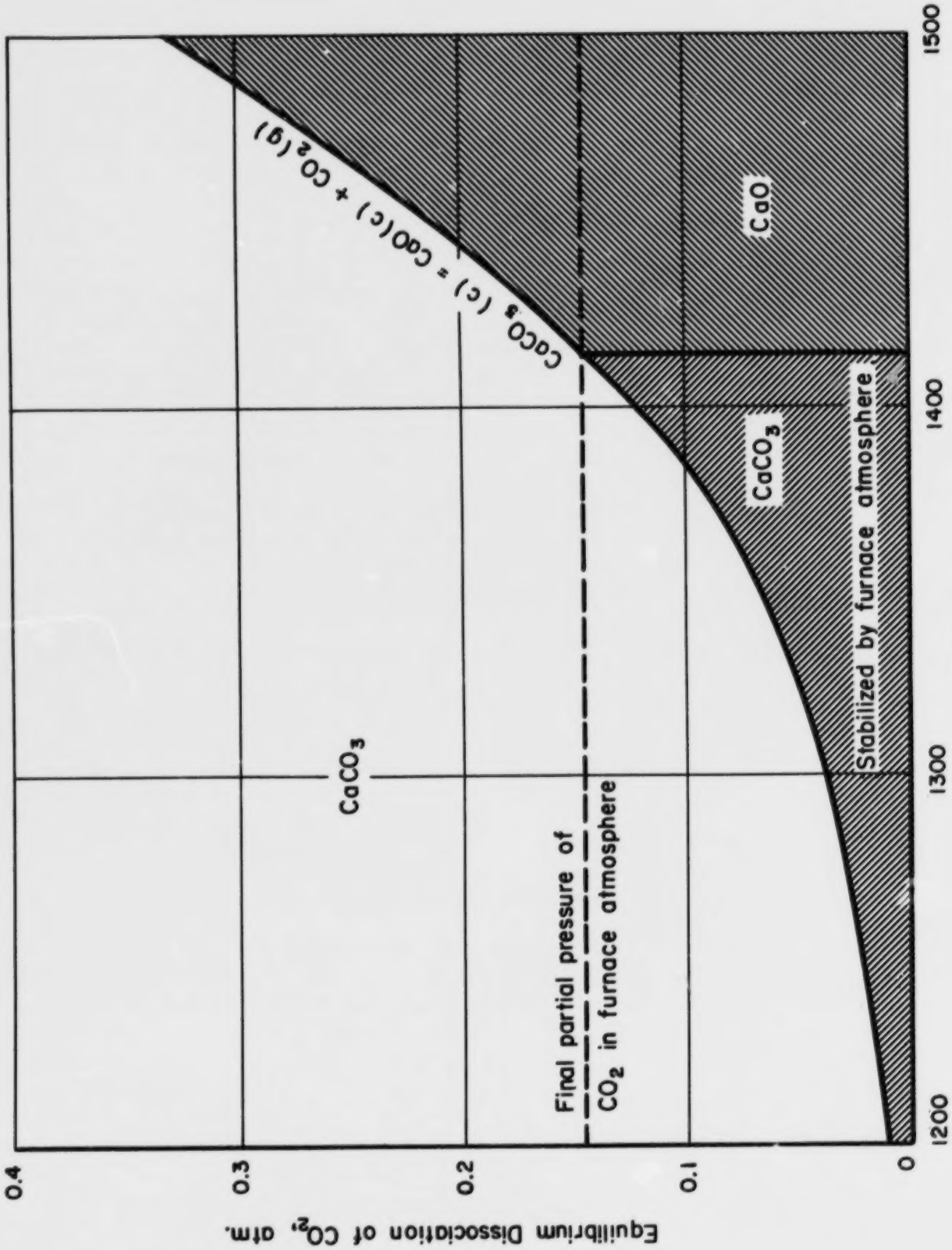

FIGURE 1. EFFECT OF FURNACE ATMOSPHERE ON DISSOCIATION OF $CaCO_3$(c)

In a flue gas containing 14.5 percent CO_2, dissociation would tend to occur approximately at 730 F. Phase equilibrium of the CaO-MgO system indicates that a double oxide forms. If this double oxide were formed in the decomposition of dolomite, then a_{CaO} would be lowered, and the desulfurizing action of lime would be decreased proportionately, as can be seen from Equation (3). Further examination of Equation (3) suggests that the desulfurizing action of CaO can be increased by lowering the activity of $CaSO_4$, as can be done by dissolving $CaSO_4$ in ash without dissolving CaO(c). This is most unlikely. The extent of desulfurizing flue gas may be affected through this means by a factor of at least four, depending on the phase equilibrium of the reaction

$$CaO(c) + SO_2(g) + \frac{1}{2} O_2(g) \rightleftharpoons CaSO_4(c).$$

Sulfite Formation

Calcium sulfite and magnesium sulfite have a thermochemical tendency to oxidize to the corresponding sulfate with excess oxygen as the data in Tables A-4 and A-5 show.

Calcium oxide will react directly with $SO_2(g)$ to form $CaSO_3(c)$ as

$$CaO(c) + SO_2(g) \rightleftharpoons CaSO_3(c).$$

This partial fixation step can lower the SO_2 concentration to 16 ppm at 1000 F and to a concentration of less than 1 ppm at 900 F under equilibrium conditions. Compared with Table 1 for the formation of $CaSO_4$, producing $CaSO_3$ has no advantages.

SO_2-O_2-SO_3 Equilibria

A driving force exists for $SO_2(g)$ to react with $O_2(g)$ to form $SO_3(g)$ up to 1400 F under standard-state conditions. This conclusion can be reached by examining the data of Table A-11. Table 4 shows calculated values of the conversion of $SO_2(g)$ to $SO_3(g)$ at equilibrium with 2.7 percent oxygen with a preponderance of $SO_3(g)$.

TABLE 4. EQUILIBRIUM CONVERSION OF $SO_2(g)$ TO $SO_3(g)$ IN FLUE GAS CONTAINING 2.7 PERCENT OXYGEN

Temperature, F	$\frac{P_{SO_2}}{P_{SO_3}}$	Approximate Equilibrium Conversion of $SO_2(g)$ to $SO_3(g)$, With 2.7 Percent Excess $O_2(g)$
748	0.01	99
876	0.10	90
1050	0.33	75

Again, it must be stressed that these are equilibrium levels. In boiler practice, nearly all the sulfur occurs as $SO_2(g)$ in the flue gas. This difference between equilibrium and real concentrations indicates a frozen equilibrium from a higher temperature where $SO_2(g)$ formation is favored. Catalysis is required to speed up the reactions sufficiently to convert the $SO_2(g)$ to $SO_3(g)$ with excess $O_2(g)$ at lower temperatures.

Sulfide Formation

Calcium sulfate or magnesium sulfate can be reduced either by excess carbon or by carbon monoxide to the corresponding sulfides upward from 800 F over the whole range of boiler temperatures. These sulfides would tend to form in the fuel-rich zone of the boiler atmosphere. The basic data for these reactions are given in Tables A-13 and A-14.

Silicate Reactions

The tendency of silica to form calcium silicate and the effect of alumina, to be discussed briefly later, illustrate how coal ash can complicate the desulfurizing action of CaO in boiler flue gas. A strong thermochemical tendency for CaO and SiO_2 to react to form silicates over the entire range of boiler temperatures exists according to the data listed in Table A-15. There is, however, a tendency for calcium silicate to react with SO_2 and O_2 to form calcium sulfate at 1400 F. These reactions may be shown as

$$Ca_2SiO_4(c) + SO_2(g) + \frac{1}{2}\,O_2(g) \rightleftharpoons CaSO_4(c) + CaSiO_3(c)$$

and

$$CaSiO_3(c) + SO_2(g) + \frac{1}{2}\,O_2(g) \rightleftharpoons CaSO_4(c) + SiO_3(c).$$

These reactions may be compared to the desulfurizing effect of CaO(c) with 2.7 percent O_2 in flue gas. The comparison can be thought of as a measure of the competition of the acidic oxides SiO_2 and $SO_2 + O_2$ for the basic oxide, CaO. Table 5 shows that $SO_2 + O_2$, essentially yielding SO_3, is the stronger acidic oxide.

TABLE 5. COMPARISON OF THE DESULFURIZING ACTION OF CaO AND CALCIUM SILICATES WITH 2.7 PERCENT O_2 IN FLUE GAS

(Unit activity assumed for condensed phases.)

Reaction	Equilibrium Concentration of $SO_2(g)$, ppm	
	1400 F	1800 F
$CaO(c) + SO_2(g) + \frac{1}{2}\,O_2(g) \rightleftharpoons CaSO_4(c)$	0.0001	1.95
$Ca_2SiO_4(c) + SO_2(g) + \frac{1}{2}\,O_2(g) \rightleftharpoons CaSiO_3(c) + CaSO_4(c)$	0.15	135.0
$CaSiO_3(c) + SO_2(g) + \frac{1}{2}\,O_2(g) \rightleftharpoons CaSO_4(c) + SiO_2(c)$	3.0	9370

Thermochemically, $CaSiO_3$ could lower SO_2 to 3 ppm at equilibrium, but the kinetics of the reaction undoubtedly would be slow at 1400 F. It is conceivable that blast-furnace slag containing CaS in a fluidized bed could desulfurize flue gas at temperatures below 1500 F. The rates of the reaction might preclude serious consideration of such a desulfurizing scheme.

Hydration of CaO(c) and MgO(c)

Basic thermochemical data for the hydration of CaO and MgO are given in Table A-16. At a water-vapor concentration of 7.1 percent by volume, as in flue gas, CaO would hydrate below 700 F, and MgO below 400 F. However, at a flue-gas concentration of 14.5 percent CO_2, CaO would already have tended to react with CO_2 to give $CaCO_3$ at 1400 F, as discussed earlier. The conclusion can be reached here that hydration or slaking of lime by steam in the flue gas will not occur.

Sodium Carbonate and Alumina

Sodium sulfate (Table A-17) is stable thermochemically above 3000 F although the table covers only the range up to 1300 F. It can be concluded that Na_2CO_3, reacting to form the sulfate, would desulfurize flue gas throughout the range of boiler temperatures. Other problems including slagging and corrosion caused by this salt eliminate further consideration of it.

Alumina could reduce $SO_2(g)$ to 1 ppm at temperatures below 800 F. This conclusion can be reached from a study of the data in Table A-17.

Ferrous Sulfate Formation

There is no thermochemical benefit of desulfurization by the addition of ferric oxide to the flue gas. Likewise, the addition of ferro-ferric oxide will not form any ferrous sulfate, except at low temperatures. These conclusions are drawn from Table A-18.

The data in Table A-19 indicate that ferrous oxide will combine with SO_2 to form ferrous sulfate at temperatures up to approximately 1700 F. Because the furnace atmosphere contains 2.7 percent oxygen, ferrous oxide will be unstable and will tend to go to the more stable ferric oxide. Therefore, ferrous oxide does not appear to be a good agent for capturing SO_2.

The data used in compiling the tables in the Appendix were taken from the most recent sources, listed in a bibliography at the end of the Appendix. The higher temperature values reported in most of the tables are extrapolated values. Because of the need for arithmetical consistency in this type of study, the significance of the values reported is beyond that which actually exists.

KINETICS OF THE SIMPLIFIED BOILER FURNACE MODEL

by

J. F. Walling, R. H. Cherry, Jr., and A. Levy

The objective of this part of the study was to attempt to identify products of the reaction of SO_2 with limestone and dolomite during the residence time available in boiler furnaces, and to estimate the rates of reaction of these substances under an assumed set of temperatures and time. The course of this task was determined largely by three facts:

(1) No pertinent chemical kinetic data on these systems which could be interpreted quantitatively were found in the literature.

(2) It is presently impossible to calculate heterogeneous reaction rates from first principles.

(3) Also, it is presently impossible to obtain reliable estimates about heterogeneous reaction rates by using data from "similar" systems.

Therefore, determination of chemical reaction rates between SO_2 and limestone or dolomite will require a laboratory effort which is not within the scope of this study.

Since it is not possible to estimate rates of reactions to calculate the probable outcome on the basis of an assumed model, shown later as Figure 2, the task was turned around. Instead, an attempt was made to provide an estimate of what the lower limit of the rate, when measured, should be in order to produce a result no poorer than heat or mass transfer control of the process if the model is adequate. Therefore, this part of the report is divided into three sections:

(1) Qualitative comments about chemical kinetics

(2) A simplified model of the furnace for purposes of kinetic calculations

(3) Estimation of reaction rate based on model for heat- and mass-transfer control.

Qualitative Chemical Kinetics

No quantitatively interpretable data on chemical kinetics for these systems were found. Information sought would have included, for example, specification of the method of chemical and physical preparation of the solid material (or other evidence to substantiate uniqueness and reproducibility), its specific surface area and density, the amount of reaction products as a function of time or flow rate, gas composition, temperature, and pressure. Some evidence of chemical stability or reproducibility of the surface of the solid with time during the reaction would also be needed.

These requirements for quantitatively interpretable data may appear to be excessively stringent. However, they have been dictated by difficult problems, well known to chemical kineticists, which are understood only in a qualitative way.(3) It may suffice to indicate here that, in heterogeneous reactions, reproducibility of the "surface phase" is critical. Any change which might alter its composition in an important average way – for example, by impurity atoms present or absent in the crystal surface, by defect structure changes, or by a strongly adsorbed species from the gas phase which may be present or absent – may profoundly alter the course of a desired heterogeneous reaction. This list is not exhaustive, and in a given instance, some changes in the surface phase may produce no observable effects on the desired reaction. However, to get reliable results, each factor must be held constant or its effect investigated in each separate instance. Some documentation of the importance of some of the effects just mentioned is available from literature pertinent to this problem.

Qualitative information found for the interaction of SO_2 with solids comes from three papers.(4, 5, 6) Perhaps the most certain conclusion to come from all three is the common report that $S^=$, $SO_3^=$, and $SO_4^=$ were all observed after reaction with SO_2 when Ca^{+2} was present. The situations in all three papers are different. In all cases, temperatures were somewhere between 750 F and 1800 F, but gas composition ranged from pure SO_2 to various air-SO_2 mixtures, and the solid varied from pure CaO or $CaCO_3$ to a rock of uncertain composition. Reaction times were much longer (minutes to tens of minutes) than those of interest in boiler furnaces (seconds). However, it seems likely that because all three anions were observed in all of the studies with their sizable diversity of conditions, it is reasonable to expect all three anions as products in boiler furnaces as well. This is the only reasonably firm conclusion which can be drawn from all these qualitative data.

However, some other inferences from these studies which are considerably more speculative are not unreasonable and may be instructive. Moreover, some of the points serve to illustrate the general statements made earlier about the kinds of factors which need control. Therefore some of this more speculative material is of interest here.

In his study of the reaction of pure SO_2 with CaO and $CaCO_3$,(5) Pechkovskii observes that:

(1) Reaction with CaO occurs appreciably at 750 F but reaction with $CaCO_3$ begins at 930 F.

(2) Reaction with CaO is nearly complete in 15 minutes, and above 1100 F the fraction of CaO reacted is much less than the fraction of $CaCO_3$.

He concludes from these observations that SO_2 reacts with $O^=$ rather than $CO_3^=$, and that the crystal perturbations caused by CO_2 evolution in $CaCO_3$ foster more rapid and complete reaction than is possible with the more stable CaO lattice.

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(3) Benson, S. W., The Foundations of Chemical Kinetics, McGraw Hill, New York (1960), Chapter XVII.
(4) Lugowska, M., "Possibility of Obtaining SO_2 From Indigenous Sulfur Ore", Przemysl Chem., 40, 95 (1960).
(5) Ketov, A. N., and Pechkovskii, V. V., "Interaction of SO_2 With CaO and $CaCO_3$", Zh. Prikl. Khim., 31 (12), 1783 (1958).
(6) Pechkovskii, V. V., "Reactions of SO_2 With Metal Oxides in an Oxidizing Atmosphere", Zh. Prikl. Khim., 30 (11), 1580 (1957).

Pechkovskii warns, however, that if O_2 is present in the gas and impurities of transition-metal oxides are present in the oxide lattice, the rates may be altered profoundly.(6) For example, he carried out two experiments identically except that in one, pure MgO was used and in the other, MgO with 9 percent Fe_2O_3 was used. The percentage conversion of the pure MgO was 5 percent and the mixed oxide conversion was 94 percent. Pechkovskii suggests as a result of such observations that if a transition-metal oxide impurity which catalyses the conversion of SO_2 to SO_3 is present, more than one path is available for an SO_2-solid reaction. The particular data on which this generalization was based involved MgO, not CaO or dolomite. However, if the interpretation is correct, it is difficult to see why it would not apply to dolomite as well, at least in a qualitative way.

It must be emphasized once again that the foregoing remarks are qualitative and speculative with respect to dolomite. Another way to support this contention is to examine factors reported to affect the rate of decomposition of limestone and dolomite. Grain size, particle surface area (roughness), heating conditions, and partial pressure of CO_2 and H_2O all affect the decomposition of $CaCO_3$. Small grains decompose more rapidly than large ones, and the larger the surface area, the greater the decomposition rate.(7) Here CO_2 reduces the rate of decomposition(8) and H_2O accelerates it(9).

Similarities are reported between the decomposition of limestone and of dolomite. For example, CO_2 is reported to retard decomposition and H_2O to accelerate it(10), just as with $CaCO_3$. However, there is at least one report of differences in rates of decomposition of one dolomite and its constituent carbonates, and of the sizable effect of small quantities of ionic impurities on the decomposition behavior of dolomite. Impurities are reported to facilitate the onset of decomposition at lower temperatures and at a generally greater rate(11). The behavior in gas-solid systems is obviously complex. The foregoing examples provide some evidence for the contention that it is impossible to estimate heterogeneous reaction rates by deduction or by "extrapolation" of known results.

In summary, it appears that:

(1) SO_2 is likely to appear in the solid phase in some distribution between $S^=$, $SO_3^=$, and $SO_4^=$ as the result of reactions in the furnace between SO_2 and limestone or dolomite.

(2) SO_2 appears to react with $CO_3^=$ after the carbonate has decomposed into $O^=$ and CO_2.

(3) If O_2 is present in the gas phase and transition-metal oxides are present in the limestone or dolomite, SO_2 may be oxidized to SO_3. Thus two paths may be available for reacting SO_2 with the solid phase.

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(8) Hyatt, E. P., Cutler, I. B , and Wadsworth, M. E., "$CaCO_3$ Decomposition in CO_2 Atmosphere", J. Am. Ceram. Soc., 41, 70 (1958).

(9) Hyatt, E. P., "Thermogravimetric Study of $CaCO_3$ Decomposition", Dissert. Abstracts, 17, 828 (1957)

(10) Bischoff, F., "On the Kinetics of the Thermal Dissociation of Dolomite and Limestone in Various Atmospheres", Z. Anorg. Chem., 262, 288 (1950).

(11) Esin, O. A., Gel'd, P. V., and Popel, S. I., "Redistribution of Ions in the Thermal Dissociation of Double Salts", Zh. Prikl. Khim., 22, 354 (1949).

(4) All of these conclusions must be speculative with respect to the SO_2-solid reaction since they are based on different chemical systems than the one of interest, on reaction times much longer than those available in boiler furnaces, and on systems which were not adequately characterized for quantitative analysis.

Simplified Furnace Model

In analyzing this system, it was necessary to model the boiler furnace after the fashion of a simple catalytic chemical reactor because heat- and mass-transfer phenomena are important. This is easily seen when it is recognized that from a practical viewpoint it would probably be desirable to inject limestone or dolomite into the system at a moderate temperature. However, the reaction with SO_2 probably does not occur appreciably below about 1000 F. Also, the contact time is short. Thus heat-up time is important. The fact that limestone and dolomite particles would not be stationary but would move with the gas stream suggests that mass transfer must be considered as well.

Two extreme cases can be envisioned. In one, heat and mass-transfer phenomena will control the rate of the process; in the other, the chemical reaction rate controls. The purpose of the model to be described presently is to estimate the effects of heat and mass transfer on the rate of the process. Since it has not been possible to estimate the chemical reaction rate, it could be assumed that heat and/or mass transfer do control the rate of the process. To the extent that the model reflects the practical situation, it can be assumed that this is the best which can be expected.

To insure that the best possible performance is obtained, it is necessary for the chemical reaction rate to be greater than that estimated on the basis of heat-mass transfer control. Therefore, within the limits of this model, an attempt was made to estimate the smallest value for the overall chemical reaction rate that would achieve the calculated performance. The procedure used was to model the gross physical situation, derive a relationship for heat transfer to an individual particle, obtain the mass transfer relationship to a particle by analogy, and solve the resulting equations.

The model assumes that the hot flue gases are flowing in a unidirectional rectangular duct that has the same cross section as the actual boiler, but which is empty and does not contain superheater or reheater tubes or other flow obstructions. The limestone or dolomite is assumed to be crushed to a uniform particle size small enough to ensure a Stokes' law flow field. That is, spherical nonporous particles are assumed with diameters less than approximately 200 microns. The assumption further specifies essentially the relative velocity between the gas and the solid particles. This relative velocity is insensitive to actual gas-flow velocity, turbulence, flow obstructions in the actual furnace, and duct geometry(12). It is assumed that the solid particles are essentially at ambient temperature when fed to the flue gas.

(12) Torobin, L. B., and Gauvin, W. H., "The Effects of Fluid Turbulence on the Particle Drag Coefficient", Can. J. Chem. Engr., 38, 189 (1960).

Heat Balance on a Particle

Since the dolomite particles are injected at ambient temperature, there is initially a large difference between the local gas temperature and the mean particle temperature. Work on radiative heat transfer to small spherical solid particles suspended in a gas led Sleicher and Churchill[13] to the result that the temperature gradient between the surface and the center of the particle is small at the temperatures of interest here. It is assumed then that no temperature gradient exists within the particle. This assumption has been used successfully by Themelis and Gauvin[14].

The differential heat balance on a single particle of diameter D_p is of the form:

$$\text{Accumulation} = \text{input} - \text{output} + \text{generation} \quad . \tag{6}$$

Individual terms in the above expression are:

$$\text{Accumulation} = (WC)_p \, (dt/d\theta)_p = (\pi \rho C D^3/6)_p \, (dt/d\theta)_p \quad , \tag{7}$$

where

W = particle weight, lb $= \frac{4}{3} \pi \frac{D_p^3}{2} \rho_p = (\pi/6) \, D_p^3 \rho_p$

C = solid specific heat, Btu/(lb)(F)

t = temperature, F

θ = time, seconds

ρ = solids density, lb/cu ft

and subscript p denotes the particles.

Heat input occurs primarily to the particle by convection (q_c).

$$q_c = h_c A_p \, (t_g - t_p) = h_c \pi \, D_p^2 \, (t_g - t_p) \quad , \tag{8}$$

where h_c is the convective heat-transfer coefficient in Btu/(hr)(ft^2)(F), A_p is the area of the particle in ft^2; and subscript g denotes the gas.

Zenz and Othmer[15] have shown that the limiting Nusselt number for heat transfer to single spheres in a Stokes' flow field is given by

$$Nu = h_c D_p / k_g = 2 \quad , \tag{9}$$

where k_g is the thermal conductivity of the gas.

The data of Johnstone et al.[16] and Joukovski[17] show a much lower limiting Nusselt number for heat transfer to clouds of small particles. Othmer and Zenz

(13) Sleicher, C. A., and Churchill, S. W., "Radiant Heating of Dispersed Particles", IEC, 48, 1819 (1956).

(14) Themelis, N. J., and Gauvin, W. H., "Heat Transfer to Clouds of Particles", Can. J. Chem. Engr., 41, 1 (1963).

(15) Zenz, F. A., and Othmer, D. F., Fluidization and Fluid-Particle Systems, Reinhold Publishing Corporation, New York (1960).

(16) Johnstone, H. F., Pigford, R. L., and Chapin, J. H., "Heat Transfer to Clouds of Falling Particles", Trans. Am. Inst. Chem. Engr., 37, 95 (1941).

(17) Joukovski, D. N., "Convective Heat Transfer Between Gases and Suspended Particles", J. Tech. Phys. (USSR), 10, 999 (1940).

concluded that the difference between the single-sphere and particle-cloud data is real, and is probably caused by interparticle hindrance effects. Consequently, the limiting value for Nusselt number is taken to be

$$\text{Nu (particle clouds)} = h_c D_p / k_g = 0.2. \tag{10}$$

After using Equation (10) in Equation (8), the convective heat transfer becomes

$$q_c = 0.2 \pi k_g D_p (t_g - t_p) \quad . \tag{11}$$

Heat losses from the particle, the output term in the heat balance, occur principally by radiation:

$$qr = \pi D_p^2 \epsilon_p \sigma (t_s^4 - t_p^4) \quad , \tag{12}$$

where

ϵ_p = particle emissivity

σ = radiation constant

t_s = temperature of the surroundings.

For this highly simplified model, it is assumed, in writing the above expression for radiative heat transfer, that:

(1) The presence of H_2O, CO_2, and CO in the flue gas has a negligible effect on the radiation rate; that is, the gas is completely transparent to all radiation.

(2) The effect on radiation transfer rates of the nonisothermal surroundings, shape factor, etc., have been ignored so that the results will be conservative.

(3) The particle sees a portion of the duct wall at some temperature below the bulk-gas temperature at a given location in the duct, and this difference between surface and gas temperatures is nearly constant throughout the duct.

It is common practice to eliminate the fourth-power temperature difference in the radiation expression by defining a radiation transfer coefficient:

$$q_r = h_r A_p (t_s - t_p) = h_r \pi D_p^2 (t_s - t_p) \quad . \tag{13}$$

Values of h_r calculated on the basis of assumptions similar to the above are available in McAdams book[18].

The generation term in Equation (6) represents the net energy released or absorbed by the overall chemical reaction as it occurs on the particle surface.

For the purposes of these calculations, the heat of the reaction will be taken as zero. This is an erroneous but not an absurd assumption. If the reaction proceeds by

(18) McAdams, W. H., Heat Transmission, Third Edition, McGraw-Hill Book Company, New York (1954).

decomposition of the $CO_3^=$ and then reaction of SO_2 with $O^=$, the first step will be endothermic and the second exothermic. Up to this point at least, the net heat effect may be nearly zero. However, the reaction may not stop at this point, and whatever actions occur are likely to be on the particle's surface. The usual tabulated bulk thermodynamic properties will not be appropriate for estimating a heat of reaction on the surface because of the difference in bulk and surface properties. Therefore, since the product distribution between $S^=$, $SO_3^=$ and $SO_4^=$ and applicable thermodynamic properties are unknown, the mathematical simplicity afforded by assuming zero heat of reaction has been used.

The energy balance of Equation (6), combined with Equations (7), (11), and (13) becomes

$$\left(\frac{\pi\rho CD^3}{6}\right)_p \left(\frac{dt}{d\theta}\right)_p = 0.2\,\pi\,k_g\,(t_g-t_p) - h_r\,\pi D_p^2\,(t_s-t_p) \quad . \tag{14}$$

It is desirable now to change the independent variable, time, θ, to gas temperature, t_g, because temperature can be specified, at least approximately as a function of distance or time along the duct,

$$(dt_p/d\theta) = (dt_p/dt_g)\,(dt_g/d\theta) \quad . \tag{15}$$

The value of $(dt_g/d\theta)$ can be estimated from the temperature-time profile assumed for the model boiler furnace and shown later in Figure 2. It is constant for each of two segments along the duct.

In addition, it is assumed that the difference between the duct wall temperature, t_s, and the local bulk-gas temperature, t_g, at any point in the duct is given by a constant, $\Delta t = t_g - t_s$. Using these assumptions, Equation (14) becomes:

$$\left[\left(\frac{dt_g}{d\theta}\right)\left(\frac{\pi\rho CD^3}{6}\right)_p\right]\left(\frac{dt_p}{dt_g}\right) = (0.2\,\pi D_p k_g)\,(t_g-t_p) - (\pi D_p^2 h_r)\,(t_g-\Delta t-t_p) \quad , \tag{16}$$

which has the form

$$q_1\,(dt_p/dt_g) = q_2\,(t_g-t_p) - q_3\,(t_g-t_p-\Delta t) \quad . \tag{17}$$

Equation (17) may be rearranged to give

$$(dt_p/dt_g) = [\,(q_2-q_3)/q_1]\,\{t_p-t_g) + (q_3/q_1)\,\Delta t \quad , \tag{18}$$

where

$$(q_2-q_3)/q_1 = \frac{6\,(0.2\,k_g - D_p h_r)}{\rho_p C_p D_p^2\,(\Delta t_g/\Delta\theta)}$$

and

$$q_3/q_1 = \frac{6\,h_r}{\rho_p C_p D_p\,(\Delta t_g/\Delta)} \quad .$$

This is the final form of the energy balance.

Mass Transfer to a Particle

To estimate the mass-transfer rates from the gas to a particle, it is necessary to use one of the analogies between heat and mass transfer. Because of the lack of data, it is assumed that the Colburn j-factor for mass transfer is equal to that for heat transfer. Thus

$$j_H = j_M \tag{19}$$

$$j_H = (Nu/RePr)\ (Pr)^{2/3}$$

$$j_n = (Gz'/RePr)\ (Sc)^{2/3}$$

therefore,

$$Gz' = Nu\ (Pr/Sc)^{2/3}\ . \tag{20}$$

In the above,

Nu = Nusself number, $h_c D_p/k_g$

Re = Reynolds number, $D_p V_p \rho_g/\mu_g$

Pr = Prandtl number, $C_p \mu_g/k_g$

Sc = Schmidt number, $\mu_g/\rho_g D_g$

Gz' = modified Graetz number = $\pi D_p \left(\frac{M_m P_m C_p}{k}\right)_g K_G$

P_m = mean pressure of nontransferring gas, atm

M_m = mean molecular weight of gas

μ_g = viscosity of the gas

K_G = overall mass-transfer coefficient, lb-moles/(hr)(ft^2) (atm driving force).

Both the Prandtl (Pr) and Schmidt (Sc) numbers for a given gas are nearly constant over a considerable temperature range. Therefore, evaluation of the ratio $(Pr/Sc)^{2/3}$ at the mean of the terminal gas temperature in the duct will provide a sufficiently good approximation for this simplified model. The Nusselt number (Nu) has been assumed to be approximately 0.2 throughout the duct. Consequently, the modified Graetz number (Gz') is approximately constant along the duct:

$$Gz' = 0.2\ (0.70/0.60)^{2/3} = 0.115. \tag{21}$$

The mass-transfer coefficient at any point in the duct is given by

$$K_G = (Gz'/\pi D_p)\ (k/M_m P_m C_p)_g\ . \tag{22}$$

The overall rate of mass transfer of SO_2 from the gas to a single particle at any point in the duct is

$$N(\text{single particle}) = K_G (P_g - P_p), \text{ lb-moles/(hr)(ft}^2), \quad (23)$$

where

P_g = local partial pressure of SO_2 in gas, atm

P_p = partial pressure of SO_2 on solid surface, taken as zero.

The total transfer of SO_2 to all the particles near a given location in the duct is approximately

$$N_T = (K_G A_T)\ P_g, \text{ lb-moles/hr}^2, \quad (24)$$

where A_T is total surface area of all particles in solid:

$$A_T = 6\ W_p/\rho_p D_p, \text{ sq ft/hr} \quad (25)$$

W_p = rate of limestone or dolomite injection by weight into flue-gas duct, lb/hr.

From Equations (22), (24), and (25), the mass-transfer [Equation (26)] emerges.

$$N_T = (G_z') \left(\frac{k}{C_p}\right)_g \left(\frac{1}{M_M P_M}\right)\left(\frac{6\ W_p}{\pi D_p^2 \rho_p}\right) P_g \ . \quad (26)$$

Rate Estimate Based on the Model for Heat- and Mass-Transfer Control

The proper method of calculation requires simultaneous solution of the heat [Equation (18)] and mass [Equation (26)] transfer equations for an increment of distance or time down the furnace. The overall result can be obtained by summing partial results from each segment.

A simpler procedure has been used here. Conservative assumptions have been made about the effects of heat transfer, and attention is focused on the mass-transfer equation. This may have introduced some inconsistencies in the model. However, it is considered that more elaborate computations are not justified.

The decrease in the SO_2 partial pressure was estimated for the following operating conditions using dolomite as an example:

(1) A total mass flow of 5475 tons/hr of which 5400 tons/hr is flue gas.

(2) The mole fraction of SO_2 is 3×10^{-3}, its weight fraction is 6.5×10^{-3}, and therefore the SO_2 mass flow is about 7000 lb/hr.

(3) Total system pressure is 1 atmosphere. The average molecular weight of the gas, 29.5, and the partial pressure of inert substances is assumed to be constant throughout the furnace.

(4) At steady-state operation, dolomite equal to 1 percent of the total flue-gas-weight flow rate is charged, so that W_p = 54 tons/hr.

(5) Spherical particles of 74-micron diameter are assumed. $D_p = 2.4 \times 10^{-4}$ ft.

(6) Dolomite has a specific gravity of approximately 3.0, so that $\rho_p = 187$ lb/ft^3.

(7) The temperature-time profile in the duct is given by Figure 2 in the next section of this report. Two linear segments are assumed to be adequate for this simplified calculation.

Mean values of specific heat and thermal conductivity of the gas are used for each segment of the duct.

Then from Equation (26)

$$\sum_{\Delta\theta} \int_{\theta}^{\theta+\Delta\theta} N_T d\theta = \text{moles } SO_2 \text{ consumed/hr} \qquad (27)$$

$$= \Sigma\, (0.74 \times 10^8) \left(\frac{k}{C_p}\right)_g P_g\, (5.56 \times 10^{-4}) \ .$$

Integrating over two segments using mean values for k/C_p in each segment yields the results shown in Table 6.

TABLE 6. SAMPLE FURNACE CALCULATION

Segment	Mean Temperature, F	$(k/C_p)_g$, lb/(hr)(ft)	N_T, moles/hr^2	Residence Time, hr	SO_2 Consumed	
					Moles/Hr	Lb/Hr
1	1600	0.154	3.4×10^4	5.56×10^{-4}	19	1200
2	900	0.123	2.3×10^4	Ditto	13	830
Total					32	2030

The SO_2 partial pressure at the end of the first segment is (0.003) (7000-1200)/7000 or 0.0025 atm. The exit partial pressure of SO_2 in the flue gas is (0.003) (4970/7000) or 0.002 atm.

It is concluded, then, that roughly 2/3 of the SO_2 would remain unreacted at the exhaust point on the basis of mass-transfer control of the process. This leads to the

expectation that considerations of chemical kinetics are secondary if the process is to be successful. Unless the poor result limited by mass transfer can be improved, considerations of chemical kinetics are pointless. Therefore, no attempt to estimate a lower limit to a chemical reaction rate is considered worthwhile at this point. Also, no attempt will be made to compute a temperature profile from the heat balance.

Examination of Equation (26) seems to suggest three ways in which the result might be improved:

(1) Increase the amount of limestone or dolomite added to the furnace

(2) Decrease particle size

(3) Increase contact time.

Equipment modifications needed to effect Item (3) are obvious and probably unacceptable. But at this stage, the validity of Items (1) and (2) as effective alternatives must be considered questionable. This is because of the possibility of overstepping the limits of validity of the model. For example, to achieve Item (1), a limestone or dolomite flow rate greater than 1 percent of the flue-gas flow rate would be required. Under these conditions, the assumption of a Stokes flow field is questionable. It is not known whether this would result in a net increase in mass transfer, since the effect of increased surface area may be more than offset by hindrance effects.

If the limestone or dolomite were ground to a finer particle size, the assumption about the limiting value for the Nusselt number would become even more critical. The value of Nusselt number used here was obtained by extrapolating data that are 25 years old. This complicates not only the heat-transfer problem but the mass-transfer analogy as well. Therefore, under these conditions, the model also becomes questionable. To attempt to clarify the situation, it would be necessary to carry out a carefully designed experimental program. Since this is beyond the scope of this task, no refinement of these calculations appears justified at this time.

Refinement of the calculation and model would require an experimental investigation of the heat- and mass-transfer behavior of solid-gas dispersions in the particle-size range below 200 microns. In the model presented here, the Nusselt number was obtained by extrapolation of data, giving a Nusselt number one-tenth that for the limiting theoretical value for heat transfer to a single sphere. The rate of mass transfer is taken from the analogy between heat and mass transport, and is based on this low value of Nusselt number. Thus the values calculated for mass transport are probably low if:

(1) The extrapolation is unwarranted

(2) The data are qualitative rather than quantitative

(3) The analogy breaks down.

For example, if the actual rate of mass transfer in a gas-solid system of this kind were 5 to 10 times the rate used here, and provided the reaction kinetics were sufficiently rapid, then most of the SO_2 in the flue gas would probably be converted. It is obvious that this question can be answered only by a well-planned and carefully conducted experimental program.

RECOMMENDATION FOR THE USE OF LIMESTONE AND DOLOMITE IN BOILER FURNACES

by

William T. Reid

Many interesting questions come up in considering the most effective way in which lime or magnesia can fix the sulfur in flue gas. Must the additive be calcined before it is injected into the flue gas? Is there a difference in the behavior of lime and magnesia, and how does dolomite compare in effectiveness with limestone? At what temperature is the fixation of sulfur most likely to be highest? What is the effect of a shift in temperature as the additive and flue gas cool in passing through superheaters, reheaters, economizers, and air heaters? Where is the best point for injecting the additive? What interaction can be expected between added limestone or dolomite and the ash in the fuel?

Intensive experimentation will be required to resolve these questions. First, however, to place such tests on a firm basis, the fundamental thermochemical parameters have been considered as they affect the overall chemical reactions between limestone and dolomite with flue gas. These calculations of the many possible reactions show which are most likely to take place and the effect on the reactions of changes in temperature and composition. Kinetic considerations based on the best available information show which factors influence the rate of SO_2 capture, and, in turn, demonstrate that mass transfer rather than chemical reaction rates probably will be the dominating factor. Such basic considerations are held as highly important in guiding later experimentation in large central-station boiler furnaces.

This section of the report relates the thermochemical and kinetics sections to the practical problems of using limestone and dolomite most effectively in boiler furnaces. It is intended mainly as a guide to future tests, either on a relatively small scale in the laboratory, or in experimentation in operating boilers. Results of the many thermochemical calculations listed in the Appendix will be helpful to others interested in exploring this problem further.

Basic Conditions

Establishment of ground rules were necessary to define the conditions on which the calculations were based. These limiting rules were fixed by factors related both to boiler furnaces and to fuels. For example, they relate to temperature, residence time as affected by mass flow rate, heat absorption, fuel characteristics, and ash analyses. It was not the intent here to analyze these individually in every case, but to arrive at overall conditions to establish broad limits for the calculations. Large deviations from these conditions probably will affect the conclusions of this study, but the results here nevertheless should provide a useful yardstick.

Composition of Flue Gas

Ultimate analyses of coal and of residual fuel will vary widely, and flue-gas composition will change with the fuel and with such operational factors as excess air. Table 7 shows the composition of flue gases chosen as typical for coal and for oil firing. Water is shown in these analyses because, of course, the temperature of the gas is above the dew point and water is uncondensed, unlike in an Orsat apparatus. For residual fuel, the lower limit for oxygen when operating with low excess air can be taken as 0. 2 percent; the other constituents are shifted proportionately.

TABLE 7. TYPICAL COMPOSITION OF FLUE GAS

	Percentage Composition		
		Residual Fuel	
	Pulverized Coal	Normal Excess Air	Low Excess Air
CO_2	14. 5	12. 2	12. 5
O_2	2. 7	2. 7	0. 2
N_2	75. 4	74. 9	76. 9
H_2O	7. 1	9. 9	10. 1
SO_2	0. 3	0. 3	0. 3
	100. 0	100. 0	100. 0

Although Table 7 shows the flue-gas composition when combustion is complete, other conditions occur within a flame. While combustion is occurring, some regions are overrich in fuel, while O_2 can be in great excess elsewhere. These transient conditions are most difficult to measure, and it is not within the scope of this study to consider such nonequilibrium conditions.

Composition of Typical Coal Ashes

The impurities in coal vary widely, with at least seven constituents affecting ash fusibility. Table 8 gives the composition of the ash from three widely differing coals, and the typical limits of each component.

Iron in these ash analyses is reported as Fe_2O_3. In coal-ash slags, where the ash has been melted to form a silicate "glass", 90 percent of the iron usually is present as FeO and 10 percent as Fe_2O_3. The state of the iron in fly ash varies widely. It is often about half FeO and half Fe_2O_3.

Sulfur trioxide shown in these analyses represents the state of the mineral matter in the coal when it has been heated to no more than 1400 F. At higher temperatures when the ash melts, all sulfur is expelled; coal-ash slags seldom contain more than 0. 1 percent SO_3.

TABLE 8. COAL-ASH ANALYSES

Component	Percentage Composition			
	Pennsylvania, Pittsburgh Bed	Kentucky, Straight Creek	Illinois, No. 6	Typical Limits
SiO_2	44.7	15.9	46.2	20-60
Al_2O_3	22.7	16.3	22.9	10-35
Fe_2O_3	17.3	52.4	7.7	5-35
CaO	6.5	5.7	10.1	1-20
MgO	0.9	1.0	1.6	3-4
Na_2O	(2.3)	(1.9)	0.7	1-4
K_2O			0.8	1-12
SO_3	6.6	6.8	8.9	
	100.0	100.0	98.9	

Composition of Oil Ash

Ash from residual fuel is entirely different from coal ash. Table 9 gives the analyses of the impurities in two residual fuels, one low and the other high in vanadium.

TABLE 9. OIL-ASH ANALYSES

Component	Percentage Composition	
	Low Vanadium (Mid-Cont.)	High Vanadium (Iran)
SiO_2	31.7	12.1
$Al_2O_3+Fe_2O_3+TiO_2$	31.8	18.1
CaO	12.6	12.7
MgO	4.2	0.2
Na_2O	6.9	--
V_2O_5	Trace	38.5
SO_3	10.8	7.0
	98.0	88.6

Occurrence of Sulfur

Sulfur in fuels varies widely, with the upper limit nominally 5 percent. In coal, sulfur occurs in three forms, with seldom more than a tenth of the total sulfur occurring as a sulfate. The remaining 90 percent or more of the sulfur is usually about evenly divided between pyritic sulfur (FeS_2) and organic sulfur associated with the coal substance. Pyrite occurs in discrete particles ranging in size from a few microns to "sulfur balls" weighing many pounds. Although pulverizers are set to reject such large chunks of pyrite, the smaller particles are not liberated when coal is ground only to 200 mesh (74 microns). Hence, much of the pyrite remains in the pulverized coal going to the burners. Irrespective of source, the major part of the sulfur in coal appears eventually in the flue gas, nearly all of it as SO_2, as noted earlier. Small amounts of sulfur may be trapped in fly ash, but usually this will not exceed 5 percent of the total sulfur originally present in the coal.

Essentially all the sulfur in oil is present as organic compounds, for example mercaptans, thiophenes, and complex sulfides. It can be removed only by such methods as hydrodesulfurization, a relatively difficult process costing at least 50 cents per barrel.

Temperature and Time

Defining gas temperatures in a system as complicated as a large boiler furnace is difficult because the system is a dynamic one; the temperature of the gas stream decreases in a complex fashion as the products of combustion move past heat-receiving surfaces. Being a dynamic system, time is also important, and it is this temperature-time factor that poses some of the problems in evaluating the fixation of SO_2 by limestone or dolomite. Corner-fired furnaces and cyclone-fired ones are quite different, and the gas temperature-time relationship also differs considerably. Similarly, the temperature pattern in a slag-tap furnace is not the same as that in a dry-bottom furnace. With oil firing, the situation is still different.

Figure 2 gives the time-temperature pattern assumed for this study. It represents a fair mean of the conditions in large boiler furnaces, although individual units might differ considerably. With it as a guide, however, the temperature range was established for the thermochemical calculations, and available reaction times were provided for the kinetic evaluations. The figure is based on the assumption that the flame reactions last 100 milliseconds, and that the products of combustion are in the furnace, in the superheat and reheat sections, and in the economizer sections for 2 seconds each, with a final 100 milliseconds in the air heater before passing to the stack. The temperatures shown are based on fair estimates expected for large steam generators.

Deposits on the heat-receiving surfaces over which the gases flow will be at some temperature intermediate between the metal temperature and the gas temperature. Furnace-wall deposits will range from about 2000 F to 2800 F, depending on position and whether the unit is slag tap or dry bottom; exposed-metal temperatures in the furnace will seldom exceed about 800 F. In superheaters, the deposits will have an average temperature of perhaps 1500 F, with exposed metal at about 1200 F. Ash deposits in superheaters and reheaters will have a maximum surface temperature of about 2000 F.

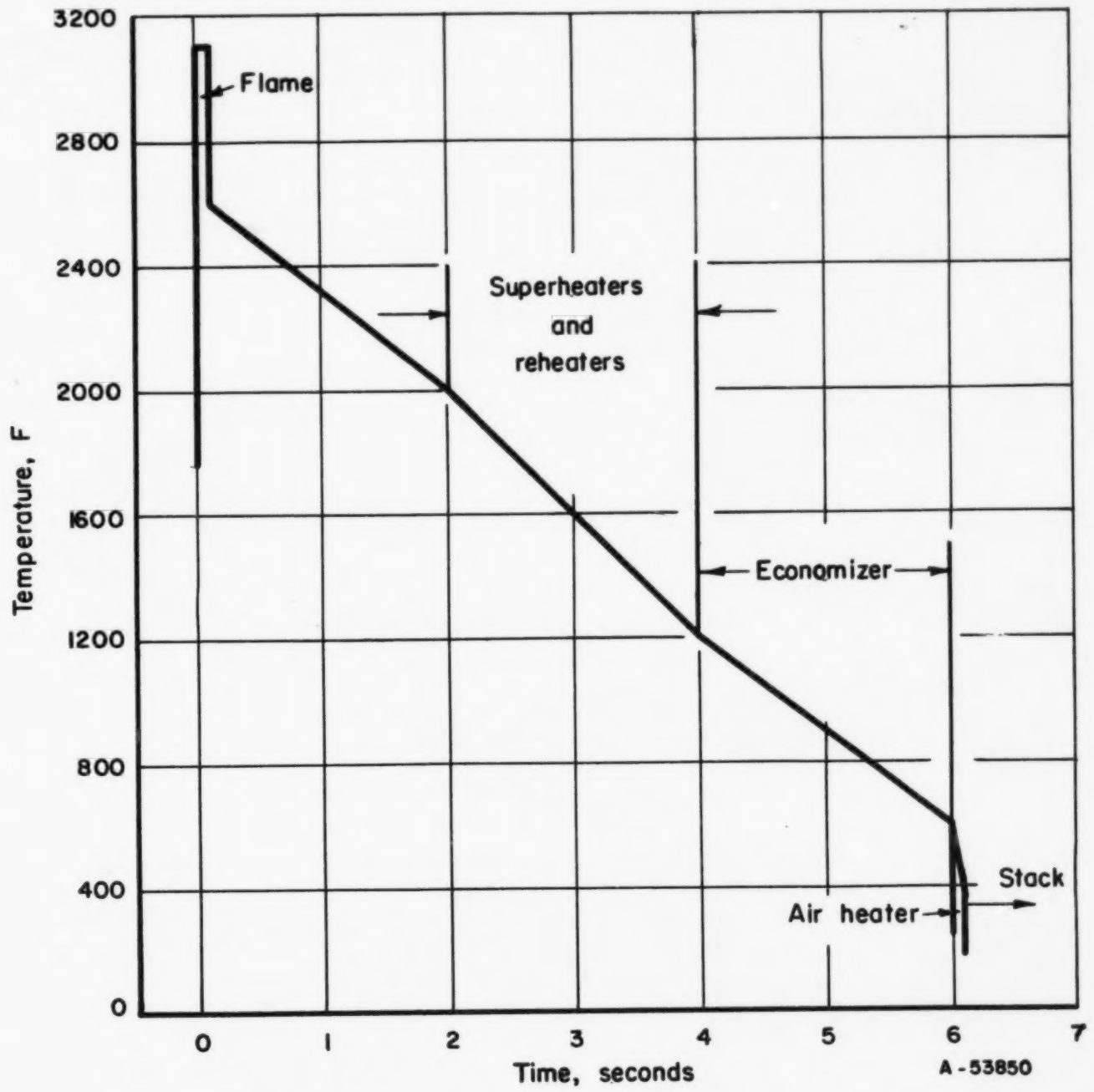

FIGURE 2. TEMPERATURE-TIME RELATIONSHIP ASSUMED FOR FLUE GAS

Reactions With Ash

As was shown in Table 2, both CaO and MgO are commonly present in coal ash and together with iron oxides make up the major fluxing constituents. Generally, more CaO is present than MgO. These oxides are also present in oil ash, usually as a greater percentage of the ash than in coal.

Although almost no work has been done on the relationship between composition and fusibility of oil ash, a great deal of effort has been spent learning how the fusibility of coal ashes depends on their composition. Particularly good relationships have been developed between the composition and the viscosity of coal-ash slags at different temperatures.[19] In addition to Newtonian viscosity, the behavior of coal-ash slags also has been investigated at lower temperatures, when the separation of a solid phase radically affects the flow behavior of the slag.[20] The findings of those studies, made more than two decades ago, have been confirmed by recent work in this country and in England.

A basic concept developed in those early studies was that the viscosity of a coal-ash slag at a given temperature, say 2600 F, depends only upon the "silica percentage" of the slag, defined as

$$\text{Silica percentage} = \frac{SiO_2}{SiO_2 + Fe_2O_3 + CaO + MgO} \times 100 \quad , \qquad (28)$$

where SiO_2, CaO, and MgO are the percentages of these components shown by a chemical analysis of the slag, and Fe_2O_3 is the percentage of iron oxides recalculated as Fe_2O_3.

Figure 3 shows how closely experimental measurements of viscosity at 2600 F are related to this silica percentage. In equation form, the relationship is

$$\log(\mu - 1) = (0.066)(SiO_2) - 1.4 \quad , \qquad (29)$$

where μ is the viscosity in poises at 2600 F, and SiO_2 is the silica percentage. Large variations in the ratio of SiO_2/Al_2O_3 and of $Fe_2O_3/CaO + MgO$ have almost no effect on the viscosity. Similarly, normal variations in Na_2O and K_2O are not important. Also of interest here is the fact that CaO and MgO can be taken as equivalent fluxes; they can be considered as a single factor in affecting viscosity, at least when the percentage of MgO is low as it usually is in coal ashes.

The major significance of the silica-percentage concept is that it shows that increasing Fe_2O_3 or CaO + MgO leads to a more fluid slag. As the flux content increases, the viscosity of the slag goes down markedly, being only 1 poise at 2600 F when the silica percentage is 30. If such a slag contained 15 percent equivalent Fe_2O_3 and 2 percent alkalies, with a SiO_2/Al_2O_3 ratio of 2, the CaO + MgO content of the original slag would have been 44.6 percent.

(19) Nicholls, P., and Reid, W. T., "Viscosity of Coal-Ash Slags", Trans. ASME, 62, 141-153 (1940).

(20) Reid, W. T., and Cohen, P., "The Flow Characteristics of Coal-Ash Slags in the Solidification Range", Trans. ASME, 66, 83-97 (1944).

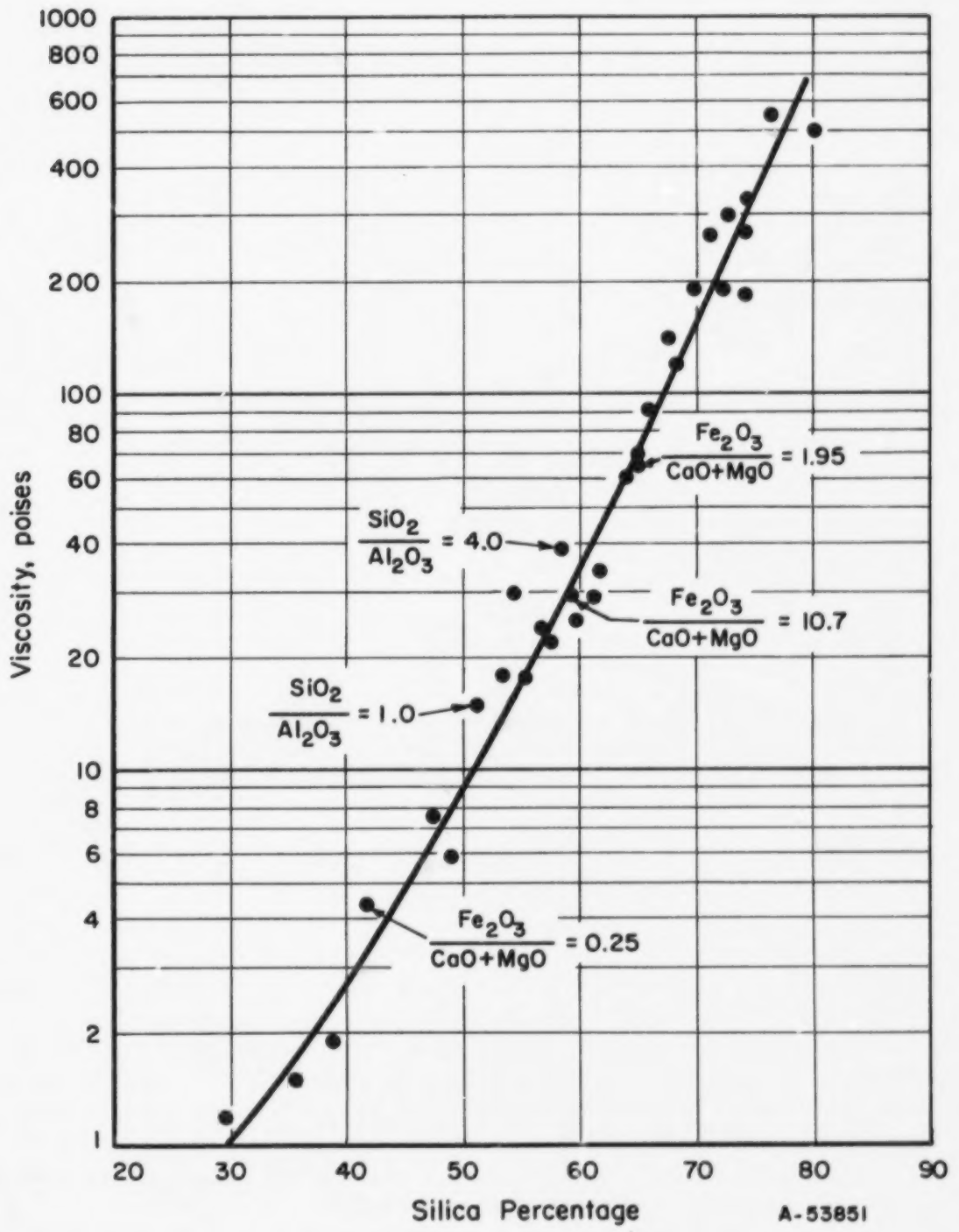

FIGURE 3. VISCOSITY OF COAL-ASH SLAGS AT 2600 F IN AIR

At some upper limit, CaO and MgO no longer serve as fluxes. Still greater amounts in coal ash result in an increase in fusibility rather than a decrease. Figure 4 illustrates how adding CaO to one coal ash decreased the "flow temperature", a measure of fusibility, until the CaO content was about 40 percent and increased the flow temperature with further additions of CaO.(21)

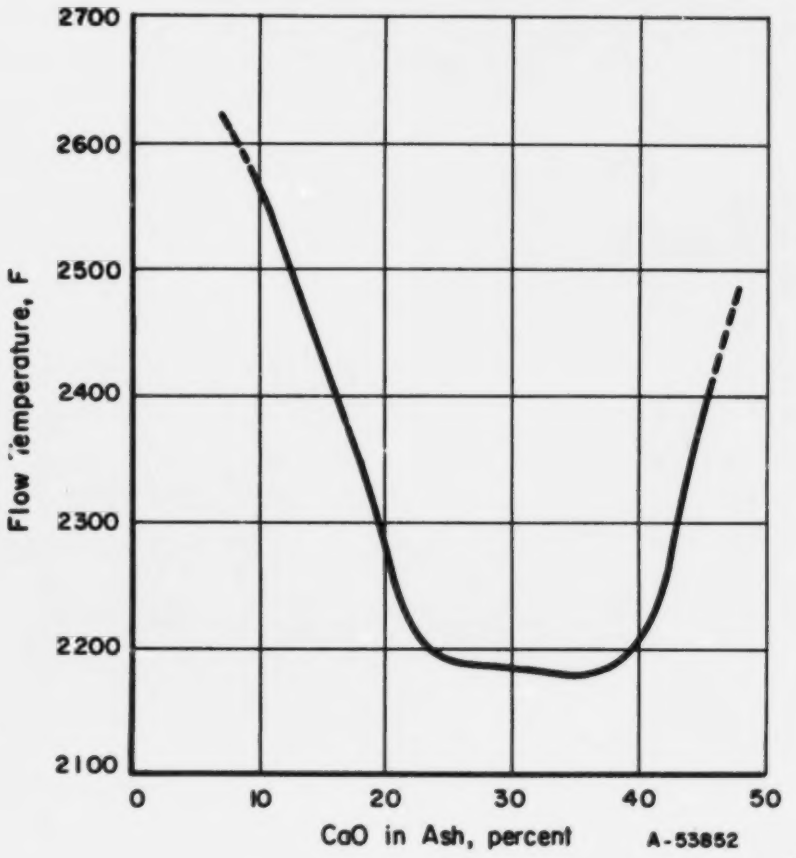

FIGURE 4. EFFECT OF LIME CONTENT ON FUSIBILITY OF COAL ASH(21)

The point of this argument is that moderate amounts of lime or dolomite added with the fuel so that there would be an intimate mixture of additive and the ash in the fuel in the furnace during combustion could lead to serious problems with slagging, particularly because temperatures would be so high in the flame that the slagging reactions could occur rapidly. If a great excess of lime or dolomite were used, so that the CaO content in the ash was greater, say, than 50 percent, the resulting slag might not cause troubles. If, however, only part of the lime or dolomite reacted with the ash so that the slag contained but 30 or 40 percent CaO, the fluidity of the resulting slag would be excessively high. This would almost certainly lead to troubles through slagging or the accumulation of sticky deposits in superheater sections.

To complicate the picture still more, Barnhart and Williams(22), in studying the sintering characteristics in the laboratory of mixtures of various additives with fly ash, showed that the sintering strength was decreased most by dolomite, CaO, and MgO in a mixture of 20 percent additive and 80 percent fly ash. It should be noted, however, that these mixtures were not heated above 2000 F. Hence, slagging reactions between

(21) Nicholls, P., and Reid, W. T., "Fluxing of Ashes and Slags as Related to the Slagging Type Furnace", Trans. ASME, 54, 167-190 (1932).

(22) Barnhart, D. H., and Williams, P. C., "The Sintering Test, An Index to Ash-Fouling Tendency", Trans. ASME, 78, 1229-1236 (1956).

the ash and the additive were unlikely, and the additive remained as a loose unreacted solid to separate the fly-ash particles and lower their sintering strength.

Further questions come from comments such as by Baley in a discussion of Barnhart and Williams's paper. He recounts how adding only 1/3 pound of MgO per ton of coal fired apparently decreased the amount of hard-bonded "eutectic" on tubes in the 1500 F zone. Assuming 10 percent ash in his coal, this amount of additive would have increased the MgO level by only 0. 2 percent, an insignificant amount.

Until more experimental evidence is in hand, it must be concluded that limestone or dolomite added through the burner with the fuel, or injected directly into the flame in boiler furnaces, can increase the fouling tendency of the coal ash by reducing the viscosity of the coal-ash slag. Great excesses of additive may overcome this slagging action, but as yet the exact action cannot be predicted. Caution should be used in planning full-scale experiments where limestone or dolomite is added to high-temperature zones. At least it should be recognized that fouling might be accentuated by the presence of CaO and MgO that has reacted, at least in part, with coal ash.

The problem is even more complicated with oil ash, lacking information on how lime or magnesia affect its fusibility. But with its much lower ash content, residual fuel is less likely to produce a low-melting slag by addition of lime or magnesia because the amount of additive necessary to capture SO_2 in flue gases would be greatly in excess of that required to "flux" the oil ash. Here, the ash in the fuel would be such a small fraction of the total deposit that the problem of increased fusibility would not arise, and the great excess of CaO would lead to refractory rather than to fusible deposits.

The thermochemical calculations clearly show in Table 5 that the conversion of CaO to Ca_2SiO_4 or $CaSiO_3$, as would be typical of reactions between added CaO and the silica in coal ash, decreases the ability of the lime to capture SO_2 by as much as four orders of magnitude. This is a great enough difference to suggest that any lime or dolomite added at temperatures high enough to produce slagging essentially would remove that additive as far as reaction with SO_2 is concerned.

Hence, from two points, the possible increase in slagging and the inability to react with SO_2, any lime or magnesia going into a coal-fired boiler furnace should be added at a temperature low enough that it will not react with the silica in the coal ash. This would eliminate adding limestone or dolomite in direct admixture with the fuel. It would also suggest that blowing the additive into the furnace at the burner level to take advantage of the high level of turbulence near the flames would be undesirable.

With oil firing, the situation would be quite different. Here the limestone or dolomite could be added directly to the fuel, although this might cause practical problems in the wear of pumps and burners. Instead, injection of the additive directly into the flame region might be more useful. Considering the low level of ash in residual fuel oil, any silica present to tie up lime and magnesia would be so small that it could be disregarded. A possible shortcoming could be that limestone and dolomite might be overburned by exposure to temperatures above 2600 F, even momentarily. If heated excessively, the resulting CaO or MgO might be physically modified so as to reduce its reactivity, as occurs with slaked lime. Because this property varies with different limestones and dolomites, and because neither the thermochemical calculations nor the kinetic evaluations give any clue to the effect of overburning, it can be considered only

as a possible shortcoming to injecting the additive directly into the hottest zones of oil-fired equipment. In general, limestone heated about 2450 F and dolomite heated to over 2250 F will be overburned and have poor reactivity.

Calcination

The desulfurizing action of limestone and dolomite before calcination is possible thermodynamically as shown by the calculations. Limestone, for example, as shown by calculations based on data in Table A-10, may be only slightly less active at 1400 F than CaO, shown in Table A-1. Even at 1000 F, limestone is not appreciably less effective than CaO, both of these materials having an extremely low level of SO_2 in the surrounding gas phase at equilibrium. Hence, at least by these calculations, it is not necessary that the limestone or dolomite be calcined to capture SO_2. Practically, however, it may prove necessary to convert the additive to CaO or MgO to achieve a feasible rate of reaction.

This same point may serve to fix the lower temperature at which CaO will be effective. Figure 1 indicates that CaO produced by heating limestone to a higher temperature will revert to $CaCO_3$ when cooled to 1415 F in flue gas containing 14.5 percent CO_2. Again, it remains to be proven by experiment whether this reversion to $CaCO_3$ will appreciably decrease the rate at which SO_2 can be captured.

Comparison of Limestone and Dolomite

Thermodynamically, at least, CaO is appreciably more effective than MgO in reacting with SO_2 under furnace conditions. As was shown in Table 1, the equilibrium concentration at 1400 F of SO_2 over CaO is only 0.001 ppm, whereas it is 180 ppm for MgO. At 1800 F, the equilibrium SO_2 level over CaO is 1.95 ppm, while it is upward of 500 ppm with MgO. Stated another way, equivalent equilibrium SO_2 levels are obtained about 400 F higher with CaO than with MgO. Because the rate of the reaction between solid and gas must be some function of temperature, even though the kinetics calculations could not develop this relationship, it follows that CaO at any given temperature could be appreciably superior to MgO for tying up SO_2. On this same basis, limestone should be better than dolomite for removing SO_2 from flue gas.

Catalytic Activity of Impurities in Limestone

The formation of $CaSO_4$ from the reaction of CaO with SO_2 implies oxidation, as is shown in Table A-1. Lime can also react with SO_2 alone to form $CaSO_3$, as illustrated by Table A-4, but the equilibrium level of SO_2 to form $CaSO_4$ at 1000 F is only 1.7×10^{-11} ppm, whereas to form $CaSO_3$, it is 16 ppm. On this basis, the oxidation step would be greatly preferred. Hence, any operation that enhances the formation of SO_3 from SO_2 will help to increase the amount of SO_2 captured, and possibly the rate as well.

Probably the simplest way of increasing the formation of $CaSO_4$ over $CaSO_3$ would be to incorporate a small quantity of Fe_2O_3 in the limestone. This Fe_2O_3, serving as a catalyst to promote the approach to equilibrium of SO_3, also would increase the rate of the overall reaction. Wahnschaffe in Germany[23], working with dolomite containing 0.7 percent Fe_2O_3, showed that desulfurization increased as additional Fe_2O_3 was added, with essentially no further appreciable gain above 2 percent total Fe_2O_3. Pechkovskii[5] also shows that transition-metal oxides present in C_2CO_3 catalyzed the conversion of SO_2 to SO_3 and increased the rate at which sulfur was captured.

Hence, limestone or dolomite containing up to perhaps 3 percent Fe_2O_3 would be preferred over purer stone containing less than 0.5 percent Fe_2O_3. Addition to limestone or dolomite of mill scale or other inexpensive sources of Fe_2O_3, preferably before grinding so as to achieve the best possible mixture, should improve the capture of SO_2.

Preferred Location in Furnaces for Addition of Limestone or Dolomite

As shown earlier, limestone or dolomite intended for the fixation of SO_2 probably should not be added with the fuel, particularly with pulverized coal containing silica in the ash. The preferred point of addition should be where the gas temperature is as high as possible consistent with minimum reaction with ash. For most coals, this temperature will be about 2000 F. Typically, this is about at the furnace outlet, or roughly at about the point where the flue gases enter the superheater and reheater sections.

The minimum temperature at which any appreciable capture of SO_2 will still occur is less easily defined, for there will be a gradual fall-off in activity as the gases cool. Practically, however, the transition of CaO to $CaCO_3$ on cooling to 1400 F in flue gas may set the lower limit. However, since $CaCO_3$ may be nearly as effective in capturing SO_2 as is CaO, as was discussed under Calcination, it is possible thermodynamically that there is no lower temperature limit. This will be an important point to check experimentally. Lacking such verification, it seems logical to conclude that the rate of SO_2 pickup will be impractically low at less than perhaps 1000 F, and that this be considered as a reasonable lower limit, as was demonstrated by Pechkovskii.[5]

This temperature analysis means, of course, that the limestone or dolomite must be added to the gas stream at the entrance to the superheater section, and that 2 or 3 seconds at most will be available before the gas stream will have been cooled below 1000 F. Table 6 shows, however, that if mass transfer controls the process as the kinetic study indicates it will, then only a third of the SO_2 would be captured in 4 seconds. As noted in that section, the situation might be improved by using more additive, grinding the additive to a smaller particle size, or increasing contact time, but how far these alternatives can be carried cannot be predicted now.

(23) Wahnschaffe, E., "Desulfurization of Flue Gases by the Dolomite Process" (PHS files, source documentation not available).

Quantity of Additive Required

For coal firing, relatively large amounts of limestone or dolomite would be required to fix all the SO_2 in the flue gas. For example, in a typical pulverized-coal-fired boiler furnace serving a 500-megawatt turbine, the amount of coal burned per day can be taken as roughly 5000 tons. With 3 percent sulfur, the total quantity of SO_2 produced per day would be 300 tons. Also, if the ash content of this coal were 10 percent, and if the ash contained 40 percent SiO_2, there would be 200 tons of SiO_2 per day passing through the furnace.

Assuming that the limestone was added at the furnace outlet so that there would be no reaction with ash, the amount needed would come to 465 tons of limestone daily to combine stoichiometrically with the SO_2. The maximum quantity of $CaSO_4$ formed would be about 640 tons daily.

If, besides the SO_2, even half the available SiO_2 in the ash were to react with the added CaO, assuming that the limestone was admixed with the fuel, then 166 more tons of limestone would be required daily to form $CaSiO_3$.

These are extraordinarily large quantities even of such an inexpensive material as limestone or dolomite. Handling this large quantity of material economically would pose some troublesome engineering problems. Hence, before any serious attempts are made to use limestone or dolomite on this huge scale, it would seem worthwhile to make smaller plant tests where these theoretical considerations could be checked.

Settling for capture of half the SO_2 in the flue gas would ease the problem appreciably, but there is no assurance as yet that stoichiometric ratios of limestone or dolomite to SO_2 would indeed fix all the SO_2 as $CaSO_4$ or $MgSO_4$. That conclusion, too, would have to be based on large-scale testing.

CONCLUSIONS

The results of this study can be summarized as follows:

- Thermochemical calculations based on the best available data show that CaO is capable, theoretically, at equilibrium of removing all but 1 ppm of SO_2 from flue gas at 1770 F.
- With MgO, the temperature can be no higher than 1200 F for an SO_2 level of 1 ppm at equilibrium.
- Increasing the temperature increases the concentration of SO_2 remaining in the flue gas, so that CaO is incapable of removing any SO_2 from a typical flue gas above 2250 F, and MgO is incapable of removing SO_2 above 1550 F.
- Limestone theoretically converts to CaO in boiler atmospheres at about 1415 F; at lower temperatures, CO_2 in the flue gas will tend to reconvert CaO into $CaCO_3$.

- Uncalcined limestone should be capable of desulfurizing flue gas. Theoretically, $CaCO_3$ can be in equilibrium with well under 1 ppm of SO_2 at 1400 F. How rapidly equilibrium can be approached is not known.

- Limestone or dolomite added with the fuel in pulverized-coal-fired boiler furnaces is apt to cause serious slagging problems, while the probable reaction of CaO with SiO_2 at furnace temperatures essentially may eliminate CaO as a means of capturing SO_2 in hot flue gases carrying suspended coal ash.

- For maximum effectiveness in coal-fired equipment, limestone or dolomite should be added at the point where the flue gas is no hotter than 2000 F, probably at the entrance to the superheater sections.

- With oil-fired furnaces where the ash content of the fuel is low, the upper temperature limit will be fixed by the tendency to overburn limestone and dolomite. Because CaO is not effective as a desulfurizer above 2250 F, and MgO above 1550 F, it would appear pointless to add limestone or dolomite at appreciably higher temperatures.

- The lower temperature limit where desulfurizing essentially would stop is not known, but 1000 F appears to be a reasonable temperature below which no further reactions may occur.

- No information is available on the rates at which limestone or dolomite might fix SO_2 in flue gas, and it does not appear possible to extrapolate such data from other systems.

- Mass transfer may be the controlling process in removing SO_2 from flue gas with suspended particulate CaO and MgO. Hence, for maximum effectiveness, the quantity of additive should be as high as is practical, its particle size should be small, and the contact time should be long.

- Large amounts of limestone or dolomite would be necessary to remove SO_2 from the flue gas of a typical boiler furnace. On the basis of stoichiometric calculations, about 230 tons of limestone would be needed daily to capture half the SO_2 emitted by the boiler furnace of a 500-megawatt unit burning a fuel with 3 percent sulfur.

- Extensive experimentation will be necessary to convert these calculations into practical design data. Most badly needed will be measurements of the rate at which SO_2 is captured at different temperatures by CaO, MgO, and raw limestone and dolomite. Lacking those experimental measurements, the calculations made here can serve only as a guide to the actions occurring in boiler furnaces.

JJW:DAP:JFW:RHC:AL:WTR/mln:js:sel

APPENDIX

THERMOCHEMICAL VALUES FOR BASIC REACTIONS IN FLUE-GAS SULFUR FIXATION

REACTIONS GIVEN IN TABLES

TABLE A-1. $CaO(c) + \frac{1}{2} S_2(g) + \frac{3}{2} O_2(g) = CaSO_4(c)$

$CaO(c) + SO_2(g) + \frac{1}{2} O_2(g) = CaSO_4(c)$

TABLE A-2. $MgO(c) + \frac{1}{2} S_2(g) + \frac{3}{2} O_2(g) = MgSO_4(c)$

$MgO(c) + SO_2(g) + \frac{1}{2} O_2(g) = MgSO_4(c)$

TABLE A-3. $CaMg(CO_3)_2(c) = CaCO_3(c) + MgCO_3(c)$

$CaMg(CO_3)_2 = CaCO_3(c) + MgO(c) + CO_2(g)$

TABLE A-4. $CaSO_3(c) + \frac{1}{2} O_2(g) = CaSO_4(c)$

$CaSO_4(c) = CaS(c) + 2O_2(g)$

TABLE A-5. $MgSO_4(c) = MgS(c) + 2O_2(g)$

$MgSO_3(c) + \frac{1}{2} O_2 = MgSO_4(c)$

TABLE A-6. $MgCO_3(c) + SO_2(g) = MgSO_3(c) + CO_2(g)$

$CaCO_3(c) + SO_2(g) = CaSO_3(c) + CO_2(g)$

TABLE A-7. $CaO(c) + SO_2(g) = CaSO_3(c)$

$CaO(c) + CO_2(g) = CaCO_3(c)$

TABLE A-8. $MgO(c) + SO_2(g) = MgSO_3(c)$

$MgO(c) + CO_2(g) = MgCO_3(c)$

REACTIONS GIVEN IN TABLES
(Continued)

TABLE A-9. $MgCO_3(c) + SO_3(g) = MgSO_4(c) + CO_2(g)$

$MgCO_3(c) + SO_2(g) + \frac{1}{2} O_2(g) = MgSO_4(c) + CO_2(g)$

TABLE A-10. $CaCO_3(c) + SO_2(g) + \frac{1}{2} O_2(g) = CaSO_4(c) + CO_2(g)$

$CaCO_3(c) + SO_3(g) = CaSO_4(c) + CO_2(g)$

TABLE A-11. $\frac{1}{2} S_2(g) + O_2(g) + SO_2(g)$

$SO_3(g) = SO_2(g) + \frac{1}{2} O_2(g)$

TABLE A-12. $CaO(c) + \frac{1}{2} S_2(g) = CaS(c) + \frac{1}{2} O_2(g)$

$MgO(c) + \frac{1}{2} S_2(g) = MgS(c) + \frac{1}{2} O_2(g)$

TABLE A-13. $4C(gr) + CaSO_4(c) = CaS(c) + 4CO(g)$

$4CO(g) + CaSO_4(c) = CaS(c) + 4CO_2(g)$

TABLE A-14. $4C(gr) + MgSO_4(c) = MgS(c) + 4CO(g)$

$4CO(g) + MgSO_4(c) = MgS(c) + 4CO_2(g)$

TABLE A-15. $2CaO(c) + SiO_2(c) = Ca_2SiO_4(c)$

$CaO(c) + SiO_2 = CaSiO_3(\alpha)$

TABLE A-16. $CaO(c) + H_2O(g) = Ca(OH)_2(c)$

$MgO(c) + H_2O(g) = Mg(OH)_2(c)$

REACTIONS GIVEN IN TABLES
(Continued)

TABLE A-17. $Na_2SO_4(c) = Na_2O(c) + SO_2(g) + \frac{1}{2} O_2(g)$

$Al_2(SO_4)_3(c) = Al_2O_3(c) + 3SO_2(g) + \frac{3}{2} O_2(g)$

TABLE A-18. $FeSO_4(c) = \frac{1}{2} Fe_2O_3(c) + SO_2(g) + \frac{1}{4} O_2(g)$

$FeSO_4(c) = \frac{1}{3} Fe_3O_4(c) + SO_2(g) + \frac{1}{2} O_2(g)$

TABLE A-19. $FeSO_4(c) = FeO(c) + SO_2(g) + \frac{1}{2} O_2(g)$

TABLE A-1. THE THERMOCHEMISTRY OF SULFUR FIXATION BY CALCIUM OXIDE

Temp, F	$CaO(c)+\frac{1}{2}S_2(g)+\frac{3}{2}O_2(g)=CaSO_4(c)$[a]		$CaO(c)+SO_2(g)+\frac{1}{2}O_2(g)=CaSO_4(c)$[a]		Temp, K
	ΔF°_R, cal mole^{-1}	Log_{10} K	ΔF°_R, cal mole^{-1}	Log_{10} K	
300	-170,095	88.045	-91,036	47.122	422.2
400	-165,381	75.644	-87,291	39.926	477.8
500	-160,683	65.846	-83,566	34.245	533.3
600	-155,987	57.887	-79,843	29.630	588.9
700	-151,317	51.317	-76,154	25.827	644.4
800	-146,658	45.787	-72,464	22.623	700.0
900	-142,023	41.077	-68,816	19.904	755.6
1000	-137,421	37.026	-65,185	17.563	811.1
1100	-132,839	33.496	-61,587	15.529	866.7
1200	-128,295	30.403	-58,018	13.749	922.2
1300	-123,776	27.664	-54,476	12.175	977.8
1400	-119,298	25.231	-50,977	10.782	1033.3
1500	-114,848	23.050	-47,496	9.532	1088.9
1600	-110,443	21.091	-44,073	8.416	1144.4
1700	-106,068	19.317	-40,658	7.404	1200.0
1800	-101,734	17.707	-37,311	6.494	1255.6
1900	-97,446	16.243	-33,985	5.665	1311.1
2000	-93,192	14.902	-30,711	4.911	1366.7
2500	-72,600[b]	9.648	-14,949[b]	1.987	1644.4
3000	-53,152	6.043	-276	0.031	1922.2

(a) Data based on Appendix References (1, 7).

(b) Melting point of $CaSO_4$ = 1723 K.

TABLE A-2. THE THERMOCHEMISTRY OF SULFUR FIXATION BY MAGNESIUM OXIDE

Temp, F	$MgO(c)+SO_2(g)+\frac{1}{2}O_2(g)=MgSO_4(c)$[a]		$MgO(c)+\frac{1}{2}S_2(g)+\frac{3}{2}O_2(g)=MgSO_4(c)$[a]		Temp,
	ΔF°_R, cal mole^{-1}	Log_{10} K	ΔF°_R, cal mole^{-1}	Log_{10} K	
300	-62,020	32.103	-133,867	69.293	422.2
400	-58,245	26.641	-130,091	59.502	477.8
500	-54,488	22.329	-126,299	51.756	533.3
600	-50,733	18.827	-122,483	45.453	588.9
700	-47,003	15.941	-118,660	40.242	644.4
800	-43,271	13.509	-114,827	35.849	700.0
900	-39,571	11.445	-112,787	32.621	755.6
1000	-35,885	9.669	-108,125	29.133	811.1
1100	-32,224	8.125	-103,486	28.094	866.7
1200	-28,588	6.775	-98,874	23.431	922.2
1300	-24,973	5.581	-94,281	21.072	977.8
1400	-21,392	4.524	-89,726	18.977	1033.3
1500	-17,823	3.577	-85,181	17.096	1088.9
1600	-14,306	2.732	-80,690	15.409	1144.4
1700	-10,793	1.966	-76,203	13.878	1200.0
1800	-7,339	1.277	-71,776	12.493	1255.6
1900	-3,903	0.651	-67,370	11.229	1311.1
2000	-511	0.082	-63,007[b]	10.075	1366.7
2500	15,905	-2.114	-41,962	5.577	1644.4
3000	31,332	-3.562	-21,738	2.471	1922.2

(a) Data based on Appendix Reference (2).

(b) $MgSO_4$ decomposes at 1397 K.

TABLE A-3. THE THERMOCHEMISTRY OF DOLOMITE DISSOCIATION

Temp, F	$CaMg(CO_3)_2(c) = CaCO_3(c) + MgCO_3(c)$ [a]		$CaMg(CO_3)_2(c) = CaCO_3(c) + MgO(c) + CO_2(g)$ [a]		Temp, K
	ΔF°_R, cal mole^{-1}	Log_{10} K	ΔF°_R, cal mole^{-1}	Log_{10} K	
300	2,602	-1.347	13,021	-6.740	422.2
400	2,558	-1.170	10,670	-4.880	477.8
500	2,513	-1.030	8,337	-3.416	533.3
600	2,469	-0.916	6,019	-2.234	588.9
700	2,424	-0.822	3,722	-1.262	644.4
800	2,380	-0.743	1,442	-0.450	700.0
900	2,336	-0.676	-817	+0.236	755.6

(a) Data based on Appendix Reference (11). Data estimated by Brewer's approximation, Appendix Reference (13).

TABLE A-4. THE THERMOCHEMISTRY OF CALCIUM SULFATE AND CALCIUM SULFIDE FORMATION

Temp, F	$CaSO_3(c) + \frac{1}{2} O_2(g) = CaSO_4(c)$ [a]		$CaSO_4(c) = CaS(c) + 2\ O_2(g)$ [b]		Temp, K
	ΔF°_R, cal mole^{-1}	Log_{10} K	ΔF°_R, cal mole^{-1}	Log_{10} K	
300	-52,182	27.011	191,634	-99.195	422.2
400	-50,875	23.269	186,892	-85.482	477.8
500	-49,515	20.291	182,165	-74.649	533.3
600	-48,115	17.855	177,444	-65.849	588.9
700	-46,699	15.837	172,745	-58.585	644.4
800	-45,279	14.136	168,059	-52.468	700.0
900	-44,891	12.984	163,423	-47.269	755.6
1000	-43,726	11.781	158,809	-42.789	811.1
1100	-42,620	10.747	154,172	-38.875	866.7
1200	-41,675	9.876	149,573	-35.445	922.2
1300	-40,602	9.074	144,998	-32.407	977.8
1400	-39,568	8.368	140,498	-29.715	1033.3
1500	-38,560	7.739	136,048	-27.305	1088.9
1600	-36,785	7.026	131,599	-25.131	1144.4
1700	-35,848	6.528	127,168	-23.159	1200.0
1800	-34,954	6.084	122,834	-21.380	1255.6
1900	-34,077	5.680	118,536	-19.758	1311.1
2000	-33,258	5.318	114,225	-18.265	1366.7
2500	-29,845	3.966	93,600	-12.439	1644.4
3000	-24,293	2.762			1922.2

(a) Data based on Appendix References (1-3, 6, 7, 9). Data estimated by Brewer's approximation, Appendix Reference (13).
(b) Data based on Appendix References (1, 4, 7). Data estimated b, Brewer's approximation, Appendix Reference (13).
Note: Melting point of CaS = 1123 K.

TABLE A-5. THE THERMOCHEMISTRY OF MAGNESIUM SULFIDE AND MAGNESIUM SULFATE FORMATION

Temp, F	$MgSO_4(c) = MgS(c) + 2\ O_2(g)$[a]		$MgSO_3(c) + \frac{1}{2} O_2 = MgSO_4(c)$[b]		Temp, K
	ΔF°_R, cal mole^{-1}	Log_{10} K	ΔF°_R, cal mole^{-1}	Log_{10} K	
300	185,710	-96.128	-53,711	27.802	422.2
400	180,870	-82.728	-52,224	23.887	477.8
500	176,053	-72.144	-50,719	20.784	533.3
600	171,236	-63.546	-49,199	18.258	588.9
700	166,452	-56.450	-47,662	16.164	644.4
800	161,665	-50.472	-46,117	14.398	700.0
900	158,011	-45.701			755.6
1000	152,051	-40.968			811.1
1100	147,348	-37.154			866.7
1200	142,821[c]	-33.845			922.2
1300	138,172	-30.882			977.8
1400	133,565	-28.249			1033.3
1500	128,968	-25.884			1088.9
1600	124,431	-23.762			1144.4
1700	119,897	-21.835			1200.0
1800	115,426	-20.090			1255.6
1900	110,973	-18.498			1311.1
2000	106,565	-17.040			1366.7
2500	85,085	-11.308			1644.4
3000	64,589	-7.343			1922.2

(a) Data based on Appendix Reference (2).
(b) Data based on Appendix References (1-3, 9).
(c) Melting point of MgS = 923 K.

TABLE A-6. THE THERMOCHEMISTRY OF SULFUR DIOXIDE FIXATION BY CALCIUM CARBONATE AND MAGNESIUM CARBONATE

Temp, F	$MgCO_3(c) + SO_2(g) = MgSO_3(c) + CO_2(g)$[a]		$CaCO_3(c) + SO_2(g) = CaSO_3(c) + CO_2(g)$[b]		Temp, K
	ΔF°_R, cal mole^{-1}	Log_{10} K	ΔF°_R, cal mole^{-1}	Log_{10} K	
300	2,110	-1.092	-12,453	6.446	422.2
400	2,091	-0.956	-12,103	5.536	477.8
500	2,056	-0.842	-11,806	4.838	533.3
600	2,016	-0.748	-11,539	4.282	588.9
700	1,957	-0.664	-11,298	3.832	644.4
800	1,908	-0.596	-11,051	3.450	700.0
900			-9,796	2.833	755.6
1000			-9,317	2.510	811.1
1100			-8,799	2.219	866.7
1200			-8,130	1.927	922.2
1300			-7,606	1.699	977.8
1400			-7,069[c]	1.495	1033.3
1500			-6,513	1.307	1088.9
1600			-6,766	1.292	1144.4
1700			-6,177	1.125	1200.0
1800			-5,601	0.975	1255.6
1900			-5,013	0.835	1311.1
2000			-4,409	0.705	1366.7
2500			-1,131	0.150	1644.4
3000			-801	0.091	1922.2

(a) Data based on Appendix References (1-3, 7, 9).
(b) Data based on Appendix References (1-3, 6, 7, 9).
(c) $CaCO_3$ thermochemically unstable in furnace atmosphere.

TABLE A-7. THE THERMOCHEMISTRY OF CALCIUM OXIDE WITH SULFUR DIOXIDE AND CARBON DIOXIDE

Temp,	$CaO(c) + SO_2(g) = CaSO_3(c)$[a]		$CaO(c) + CO_2(g) = CaCO_3(c)$[b]		Temp,
F	ΔF°_R, cal mole^{-1}	Log_{10} K	ΔF°_R, cal mole^{-1}	Log_{10} K	K
300	-38,854	20.112	-26,401	13.666	422.2
400	-36,416	16.656	-24,313	11.120	477.8
500	-34,051	13.954	-22,245	9.116	533.3
600	-31,729	11.775	-20,190	7.492	588.9
700	-29,454	9.989	-18,156	6.157	644.4
800	-27,185	8.487	-16,134	5.037	700.0
900	-23,925	6.920	-14,129	4.086	755.6
1000	-21,459	5.782	-12,143	3.272	811.1
1100	-18,967	4.783	-10,168	2.564	866.7
1200	-16,343	3.873	-8,213	1.946	922.2
1300	-13,874	3.101	-6,268	1.401	977.8
1400	-11,409	2.413	-4,340	0.918	1033.3
1500	-8,936	1.793	-2,423	0.486	1088.9
1600	-7,289	1.392	-523	0.100	1144.4
1700	-4,810	0.876	1,367	-0.249	1200.0
1800	-2,357	0.410	3,244	-0.565	1255.6
1900	92	-0.015	5,105	-0.851	1311.1
2000	2,548	-0.407	6,957	-1.112	1366.7
2500	14,896	-1.980	16,027	-2.130	1644.4
3000	24,017	-2.731	24,818	-2.822	1922.2

(a) Data based on Appendix References (1-3, 6, 9). Data estimated by Brewer's approximation, Appendix Reference (13).
(b) Data based on Appendix References (1, 7).

TABLE A-8. THE THERMOCHEMISTRY OF MAGNESIUM OXIDE REACTING WITH SULFUR DIOXIDE AND CARBON DIOXIDE

Temp,	$MgO(c) + SO_2(g) = MgSO_3(c)$[a]		$MgO(c) + CO_2(g) = MgCO_3(c)$[b]		Temp,
F	ΔF°_R, cal mole^{-1}	Log_{10} K	ΔF°_R, cal mole^{-1}	Log_{10} K	K
300	-8,309	4.301	-10,419	5.393	422.2
400	-6,021	2.754	-8,112	3.710	477.8
500	-3,769	1.544	-5,825	2.387	533.3
600	-1,534	0.569	-3,550	1.317	588.9
700	659	-0.223	-1,298	0.440	644.4
800	2,846	-0.888	938	-0.293	700.0
900			3,153	-0.912	755.6

(a) Data based on Appendix References (1-3, 9). Data estimated by Brewer's approximation, Appendix Reference (13).
(b) Data based on Appendix References (1, 7).

TABLE A-9. THE THERMOCHEMISTRY OF MAGNESIUM CARBONATE REACTING WITH SULFUR OXIDES

Temp, F	$MgCO_3(c) + SO_3(g) = MgSO_4(c) + CO_2(g)$[a]		$MgCO_3(c) + SO_2(g) + \frac{1}{2} O_2(g) = MgSO_4(c) + CO_2(g)$[b]		Temp, K
	ΔF°_R, cal mole^{-1}	Log_{10} K	ΔF°_R, cal mole^{-1}	Log_{10} K	
300	-37,615	19.470	-51,601	26.710	422.2
400	-37,389	17.101	-50,133	22.930	477.8
500	-37,151	15.224	-48,663	19.942	533.3
600	-36,898	13.693	-47,183	17.510	588.9
700	-36,625	12.421	-45,705	15.500	644.4
800	-36,331	11.343	-44,209	13.802	700.0

(a) Data based on Appendix References (2, 7, 9).
(b) Data based on Appendix References (2, 7).

TABLE A-10. THE THERMOCHEMISTRY OF CALCIUM CARBONATE REACTING WITH SULFUR OXIDES

Temp, F	$CaCO_3(c) + SO_2(g) + \frac{1}{2} O_2(g) = CaSO_4(c) + CO_2(g)$[a]		$CaCO_3(c) + SO_3(g) = CaSO_4(c) + CO_2(g)$[b]		Temp, K
	ΔF°_R, cal mole^{-1}	Log_{10} K	ΔF°_R, cal mole^{-1}	Log_{10} K	
300	-64,635	33.457	-50,649	26.217	422.2
400	-62,978	28.805	-50,234	22.976	477.8
500	-61,321	25.129	-49,809	20.411	533.3
600	-59,654	22.138	-49,369	18.321	588.9
700	-57,997	19.669	-48,917	16.589	644.4
800	-56,330	17.586	-48,452	15.127	700.0
900	-54,687	15.817	-49,208	14.232	755.6
1000	-53,043	14.292	-47,621	12.831	811.1
1100	-51,419	12.965	-47,216	11.905	866.7
1200	-49,805	11.803	-46,955	11.127	922.2
1300	-48,208	10.775	-46,552	10.404	977.8
1400	-46,637[c]	9.864	-46,176[c]	9.766	1033.3
1500	-45,073	9.046	-45,810	9.194	1088.9
1600	-43,551	8.317	-45,462	8.682	1144.4
1700	-42,025	7.653	-45,107	8.215	1200.0
1800	-40,555	7.059	-44,782	7.794	1255.6
1900	-39,090	6.516	-44,464	7.411	1311.1
2000	-37,667	6.023	-44,216	7.070	1366.7
2500	-30,976	4.117			1644.4
3000	-25,094	2.853			1922.2

(a) Data based on Appendix References (1, 7).
(b) Data based on Appendix References (2, 7, 9).
(c) $CaCO_3$ thermochemically unstable in furnace atmosphere.

TABLE A-11. THE THERMOCHEMISTRY OF SULFUR AND OXYGEN AS GASES

Temp, F	$\frac{1}{2} S_2 (g) + O_2 (g) = SO_2(g)$[a] ΔF°_R, cal mole^{-1}	$\frac{1}{2} S_2 (g) + O_2 (g) = SO_2(g)$[a] $Log_{10} K$	$SO_3(g) = SO_2(g) + \frac{1}{2} O_2(g)$[b] ΔF°_R, cal mole^{-1}	$SO_3(g) = SO_2(g) + \frac{1}{2} O_2(g)$[b] $Log_{10} K$	Temp, K
300	-71,942	37.239	13,986	-7.239	422.2
400	-71,928	32.899	12,744	-5.829	477.8
500	-71,879	29.455	11,512	-4.717	533.3
600	-71,805	26.647	10,285	-3.817	588.9
700	-71,689	24.313	9,080	-3.079	644.4
800	-71,562	22.342	7,878	-2.460	700.0
900	-73,216	21.176	5,479	-1.584	755.6
1000	-72,240	19.464	5,422	-1.461	811.1
1100	-71,262	17.969	4,203	-1.060	866.7
1200	-70,434	16.691	2,850	-0.675	922.2
1300	-69,460	15.524	1,656	-0.370	977.8
1400	-68,490	14.485	461	-0.098	1033.3
1500	-67,520	13.551	-737	0.148	1088.9
1600	-66,552	12.709	-1,911	0.365	1144.4
1700	-65,582	11.944	-3,082	0.561	1200.0
1800	-64,614	11.246	-4,227	0.736	1255.6
1900	-63,647	10.609	-5,374	0.896	1311.1
2000	-62,681	10.023	-6,549	1.047	1366.7
2500	-57,867	7.691			1644.4
3000	-53,070	6.034			1922.2

(a) Data based on Appendix Reference (2).

(b) Data based on Appendix References (2, 9).

TABLE A-12. THE THERMOCHEMISTRY OF CALCIUM OXIDE AND MAGNESIUM OXIDE WITH SULFUR GAS

Temp, F	$CaO(c) + \frac{1}{2} S_2(g) = CaS(c) + \frac{1}{2} O_2(g)$[a] ΔF°_R, cal mole^{-1}	$CaO(c) + \frac{1}{2} S_2(g) = CaS(c) + \frac{1}{2} O_2(g)$[a] $Log_{10} K$	$MgO(c) + \frac{1}{2} S_2(g) = MgS(c) + \frac{1}{2} O_2(g)$[b] ΔF°_R, cal mole^{-1}	$MgO(c) + \frac{1}{2} S_2(g) = MgS(c) + \frac{1}{2} O_2(g)$[b] $Log_{10} K$	Temp, K
300	21,539	-11.149	51,748	-26.786	422.2
400	21,511	-9.839	50,697	-23.188	477.8
500	21,483	-8.804	49,686	-20.361	533.3
600	21,456	-7.962	48,698	-18.072	588.9
700	21,428	-7.267	47,760	-16.197	644.4
800	21,400	-6.681	46,832	-14.621	700.0
900	21,400	-6.189	45,224	-13.080	755.6
1000	21,388	-5.763	43,926	-11.735	811.1
1100	21,333	-5.379	43,862	-11.059	866.7
1200	21,278	-5.042	43,799	-10.379	922.2
1300	21,222	-4.743	43,739	-9.776	977.8
1400	21,200	-4.484	43,683	-9.239	1033.3
1500	21,200	-4.255	43,625	-8.755	1088.9
1600	21,156	-4.040	43,573	-8.322	1144.4
1700	21,100	-3.843	43,522	-7.926	1200.0
1800	21,100	-3.673	43,473	-7.567	1255.6
1900	21,090	-3.515	43,423	-7.238	1311.1
2000	21,033	-3.363	43,373	-6.936	1366.7
2500	21,000	-2.791	43,123	-5.731	1644.4
3000	21,000	-2.388	42,851	-4.872	1922.2

(a) Data based on Appendix Reference (4).

(b) Data based on Appendix Reference (2).

Note: Melting point of CaS = 1123 K; melting point of MgS = 923 K.

TABLE A-13. THE THERMOCHEMISTRY OF THE REDUCTION OF CALCIUM SULFATE BY CARBON AND CARBON MONOXIDE

Temp,	$4C\ (gr) + CaSO_4(c) = CaS(c) + 4CO(g)$[a]		$4CO(g) + CaSO_4(c) = CaS(c) + 4CO_2(g)$[a]		Temp,
F	ΔF°_R, cal mole^{-1}	Log_{10} K	ΔF°_R, cal mole^{-1}	Log_{10} K	K
800	1,939	-0.605	-43,821	13.681	700
1700	-81,432	14.830	-42,872	7.808	1200
2600	-160,228	20.598	-39,428	5.069	1700

(a) Data based on Appendix References (2, 4, 7).

TABLE A-14. THE THERMOCHEMISTRY OF THE REDUCTION OF MAGNESIUM SULFATE BY CARBON AND CARBON MONOXIDE

Temp,	$4C(gr) + MgSO_4(c) = MgS(c) + 4CO(g)$[a]		$4CO(g) + MgSO_4(c) = MgS(c) + 4CO_2(g)$[a]		Temp,
F	ΔF°_R, cal mole^{-1}	Log_{10} K	ΔF°_R, cal mole^{-1}	Log_{10} K	K
800	-4,207	1.313	-50,503	15.767	700
1700	-88,299	16.081	-50,631	9.221	1200

(a) Data based on Appendix Reference (2).

TABLE A-15. THE THERMOCHEMISTRY OF FORMATION OF CALCIUM SILICATES

Temp,	$2CaO(c) + SiO_2(c) = Ca_2SiO_4(c)$[a]		$CaO(c) + SiO_2 = CaSiO_3(\alpha)$[a]		Temp,
F	ΔF°_R, cal mole^{-1}	Log_{10} K	ΔF°_R, cal mole^{-1}	Log_{10} K	K
300	-30,710	15.896	-21,249	10.999	422.2
400	-30,770	14.074	-21,243	9.716	477.8
500	-30,840	12.638	-21,236	8.702	533.3
600	-30,910	11.471	-21,229	7.878	588.9
700	-30,970	10.503	-21,223	7.198	644.4
800	-31,040	9.691	-21,216	6.624	700.0
900	-31,110	8.998	-21,209	6.134	755.6
1000	-31,170	8.398	-21,203	5.713	811.1
1100	-31,240	7.877	-21,196	5.345	866.7
1200	-31,310	7.419	-21,189	5.021	922.2
1300	-31,370	7.011	-21,183	4.734	977.8
1400	-31,440	6.649	-21,176	4.479	1033.3
1500	-31,510	6.324	-21,169	4.248	1088.9
1600	-31,570	6.028	-21,163	4.041	1144.4
1700	-31,640	5.762	-21,156	3.853	1200.0
1800	-31,710	5.519	-21,149	3.681	1255.6
1900	-31,770	5.296	-21,143	3.524	1311.1
2000	-31,840	5.091	-21,136	3.380	1366.7
2500	-32,173	4.276			1644.4

(a) Data based on Appendix Reference (5).

TABLE A-16. THE THERMOCHEMISTRY OF HYDRATION OF CALCIUM OXIDE AND MAGNESIUM OXIDE

Temp, F	$CaO(c) + H_2O(g) = Ca(OH)_2(c)$[a] ΔF°_R, cal mole^{-1}	Log_{10} K	$MgO(c) + H_2O(g) = Mg(OH)_2(c)$[b] ΔF°_R, cal mole^{-1}	Log_{10} K	Temp, K
300	-10,882	5.633	-4,165	2.156	422.2
400	-8,956	4.096	-2,197	1.005	477.8
500	-7,061	2.894	-261	0.107	533.3
600	-5,190	1.926	1,658	-0.615	588.9
700	-3,347	1.135			644.4
800	-1,526	0.476			700.0
900	272	-0.079			755.6
1000	2,042	-0.550			811.1

(a) Data based on Appendix References (1, 7).
(b) Data based on Appendix Reference (2).

TABLE A-17. THE THERMOCHEMISTRY OF DISSOCIATION OF SODIUM SULFATE AND ALUMINUM SULFATE

Temp, F	$Na_2SO_4(c) = Na_2O(c) + SO_2(g) + \frac{1}{2}O_2(g)$[a] ΔF°_R, cal mole^{-1}	Log_{10} K	$Al_2(SO_4)_3(c) = Al_2O_3(c) + 3SO_2(g) + \frac{3}{2}O_2(g)$[b] ΔF°_R, cal mole^{-1}	Log_{10} K	Temp, K
300	132,791	-68.736	120,881	-62.571	422.2
400	125,436	-57.373	109,371	-50.025	477.8
500	118,081	-48.388	97,967	-40.146	533.3
600	110,719	-41.088	86,628	-32.148	599.9
700	103,365	-35.055	75,389	-25.567	644.4
800	96,010	-29.974	64,210	-20.046	700.0
900	88,655	-25.642	53,106	-15.360	755.6
1000	81,300	-21.905	42,096	-11.342	811.1
1100	73,945	-18.645	31,134	-7.851	866.7
1200	66,591	-15.781	20,261	-4.801	922.2
1300	59,236	-13.239	9,431	-2.108	977.8
1400	--	--	-1,316	0.278	1033.3

(a) Data based on Appendix Reference (1). Data estimated by Brewer's approximation, Appendix Reference (13).
(b) Data based on Appendix References (1, 7).

TABLE A-18. THE THERMOCHEMISTRY OF FERRIC SULFATE TO FERRIC OXIDE AND FERRO-FERRIC OXIDE

Temp, F	$FeSO_4(c) = \frac{1}{2}Fe_2O_3(c) + SO_2(g) + \frac{1}{4}O_2(g)$[a]		$FeSO_4(c) = \frac{1}{3}Fe_3O_4(c) + SO_2(g) + \frac{1}{2}O_2(g)$[a]		Temp, K
	ΔF°_R, cal mole^{-1}	Log_{10} K	ΔF°_R, cal mole^{-1}	Log_{10} K	
300	27,551	-14.261	34,390	-17.801	422.2
400	24,399	-11.160	30,960	-14.161	477.8
500	21,252	-8.709	27,535	-11.284	533.3
600	18,099	-6.717	24,105	-8.945	588.9
700	14,953	-5.071	20,681	-7.014	644.4
800	11,800	-3.684	17,250	-5.385	700.0
900	8,648	-2.501	13,820	-3.997	755.6
1000	5,501	-1.482	10,395	-2.801	811.1
1100	2,348	-0.592	6,965	-1.756	866.7
1200	-799	0.189	3,540	-0.839	922.2
1300	-3,951	0.883	110	-0.024	977.8
1400	-7,098	1.501	-3,315	0.701	1033.3
1500	-10,251	2.057	-6,745	1.354	1088.9
1600	-13,397	2.558	-10,169	1.942	1144.4
1700	-16,550	3.014	-13,600	2.477	1200.0
1800	-19,702	3.429	-17,030	2.964	1255.6
1900	-22,849	3.809	-20,455	3.409	1311.1
2000	-26,002	4.158	-23,885	3.819	1366.7
2500	-41,747	5.548	-41,020	5.452	1644.4
3000	-47,499	6.537	-58,160	6.612	1922.2

(a) Data based on Appendix References (1, 7). Data estimated by Brewer's approximation, Appendix Reference (13).

TABLE A-19. THE THERMOCHEMISTRY OF DISSOCIATION OF FERROUS SULFATE TO FERROUS OXIDE

Temp, F	$FeSO_4(c) = FeO(c) + SO_2(g) + \frac{1}{2}O_2(g)$[a]		Temp, K
	ΔF°_R, cal mole^{-1}	Log_{10} K	
300	55,608	-28.784	422.2
400	51,600	-23.601	477.8
500	47,600	-19.506	533.3
600	43,592	-16.177	588.9
700	39,592	-13.427	644.4
800	35,584	-11.109	700.0
900	31,476	-9.133	755.6
1000	27,576	-7.430	811.1
1100	23,569	-5.943	866.7
1200	19,568	-4.637	922.2
1300	15,560	-3.478	977.8
1400	11,560	-2.445	1033.3
1500	7,552	-1.516	1088.9
1600	3,552	-0.678	1144.4
1700	-456	0.063	1200.0

(a) Data based on Appendix References (1, 7). Data estimated by Brewer's approximation, Appendix Reference (13).

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TABLE A-29. THE THERMOCHEMISTRY OF CALCIUM HYDROXIDE REACTING WITH SULFUR DIOXIDE TO FORM CALCIUM SULFITE AND WATER VAPOR(a)

$$Ca(OH)_2(c) + SO_2(g) \rightarrow CaSO_3(c) + H_2O(g)$$

Temperature, F	E_{RT}, cal/mole	$\log_{10}K$	Temperature, K
300	-27,952	+14,478	422.2
400	-27,460	+12,359	477.8
500	-26,900	+11,060	533.3
600	-26,349	+9,848	588.9
700	-25,797	+8,693	644.4
800	-25,234	+7,610	700.0
900	-24,677	+6,598	755.6
1000	-24,501	+6,352	811.1

(a) Thermodynamic data from Table A-18.

Both compounds are extremely good desulfurizing agents if equilibrium can be approached. However, $Ca(OH)_2$ has a lower thermodynamic efficiency than an equivalent amount of CaO, as is evident from the data in Table A-21. If $Ca(OH)_2$ proves to be more effective as a desulfurizing agent than CaO, the behavior can be explained best on the basis of a more reactive physical state of CaO resulting from dehydration of $Ca(OH)_2$, not one of greater thermodynamic efficiency.

The likely reaction product of CaO or $Ca(OH)_2$ with SO_2 is $CaSO_3$. As was shown in Table A-4, $CaSO_3$ will be thermochemically reactive with the excess O_2 in flue gas to form $CaSO_4$.

TABLE A-21. COMPARISON OF CALCULATED EQUILIBRIUM CONCENTRATION OF $SO_2(g)$, ppm IN FLUE GAS, IN THE PRESENCE OF EXCESS $Ca(OH)_2$ OR CaO

Temperature, F	$Ca(OH)_2 + SO_2(g) \rightleftarrows CaSO_3(c) + H_2O$ With 7.1% H_2O in Flue Gas and Unit Activity of Solids	$CaO(c) + SO_2(g) \rightleftarrows CaSO_3(c)$ Activity of Solids Assumed to be Unity
300	2.4×10^{-10}	7.7×10^{-15}
500	2.0×10^{-8}	1.1×10^{-8}
700*	1.0×10^{-4}	1.0×10^{-4}
800*	6.9×10^{-4}	3.3×10^{-3}

*Above dissociation temperature of $Ca(OH)_2$ in flue gas.

Reliability of Calculations

A question has been raised about the reliability of these thermochemical calculations. How precisely do they define the actual equilibrium concentrations, and how reliably can the calculations be used?

The thermodynamic working Tables A-1 through A-20 were compiled and calculated from the most reliable data given in recent sources, as listed under the references given on pages A-13 and A-14. Because of the need for arithmetical consistency in this type of study, the number of significant figures in the values reported is beyond that which actually exists.

In several of the tables, high-temperature heat-capacity data were not available. In these cases, Brewer's Approximation (Reference 13) was used. Brewer's Approximation gave data comparable with that reported in Table A-1, which is based on experimental values to 2000 F. It is believed that the calculations listed in the tables can be rated as "good" for evaluating practical temperature limits of the desulfurizing action of the compounds under consideration. By estimating the limits of error for several important cases, it was concluded that the SO_2 concentration calculated at a specific temperature should not vary from the actual value by more than 10 ppm SO_2. Considering that flue gas nominally contains 2000 ppm to 3000 ppm SO_2 and that a good desulfurizer would lower the SO_2 only to 200 ppm to 300 ppm, these calculations are considered to be well within reasonable practical limits.